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PREFACE.

THIS volume contains sections on two important subjects which were not dealt with in Volumes I. and II.—namely, those on Agricultural Chemistry and on Foods. In these sections the literature of the past three or four years is dealt with; the other sections are mainly confined to a review of the literature of 1918.

The compilers of the sections on ceramics, building materials, and fermentation industries were unable to send in their copy in time for inclusion in this volume, but it is hoped to publish their reports on these subjects, together with those for 1919, in the next volume.

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ABBREVIATIONS USED IN FOOTNOTES.

THE following is a list of journals &c. to which reference is made in this volume, with the abbreviations used. Where the title has not been abbreviated it is given in the first column only.

Aberdeen Coll. of Agric. Bull.	Aberdeen College of Agriculture Bulletin.
Agric. Bull. F.M.S.	Agricultural Bulletin of the Federated Malay States.
Agric. Gaz. Canada	Agricultural Gazette of Canada.
Agric. J. India	Agricultural Journal of India.
Agric. Research Inst. Pusa Bull.	Agricultural Research Institute, Pusa, Bulletin.
Alkali Works Rep.	Reports of the Chief Inspector under the Alkali Works Act.
Amer. Electrochem. Soc.	American Electrochemical Society.
Amer. Gas Inst. News	American Gas Institute News.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst.	
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. Analyt.	Annales de Chimie Analytique.
Ann. Falsif.	Annales des Falsifications.
Ann. du Musée Colon. de Marseille	Annales du Musée Coloniale de Marseille.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Rep.	Annual Reports of the Progress of Applied Chemistry.
Ann. Rep. Rothamsted Expt. Sta.	Annual Reports of Rothamsted Experiment Station.
Apoth.-Zeit.	Apotheker-Zeitung.
Arch. Exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. f. d. ges. Physiol.	Archiv für die gesammte Physiologie der Menschen und der Tiere.
Arch. Néerl. Physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. Phys. Nat.	Archives des Sciences Physiques et Naturelles.
Archief Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Assoc. M. of S. D. Works	Association of Managers of Sewage Disposal Works.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deuts. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft.
Berl. klin. Wochenschr.	Berliner klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationeller Landwirtschafts-Betrieb.
Biochem. J.	Biochemical Journal.
Biochem. Zeits.	Biochemische Zeitschrift.

Blast Furnace and Steel Plant.	
Board of Trade J.	Board of Trade Journal.
Bot. Gaz.	Botanical Gazette.
Brasserie et Malterie.	
Brau- u. Malzind.	Brau- und Malzindustrie.
Brit. J. Phot.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Bull. Agric. Intell.	Bulletin of the Bureau of Agricultural Intelligence and Plant Diseases.
Bull. A.I.M.E.	Bulletin of the American Institute of Mining Engineers.
Bull. Écon. de l'Indochine	Bulletin Économique de l'Indochine.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. Chim.	Bulletin de la Société Chimique de France.
Caoutchouc et Guttapercha.	
Ceram. Soc.	Ceramic Society.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. News	Chemical News.
Chem. Soc. Trans.	Transactions of the Chemical Society.
Chem. Trade J.	Chemical Trade Journal.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Comptes rend.	Comptes rendus hebdomadaire des Séances de l'Academie des Sciences.
Chem. Umschau	Chemische Umschau ueber die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Coll.	Collegium.
Comm. Central Rubber Stat. Buitenzorg	Communications of the Central Rubber Station, Buitenzorg, Java.
Comm. Netherland Govt. Inst. for advising Rubber Trade	Communications of the Netherland Government Institute for Advising the Rubber Trade and Rubber Industry.
Engineer.	
Engineering.	
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News Record	Engineering News Record.
Färber-Zeit.	Färber-Zeitung.
Gas J.	Gas Journal.
Gas World.	
Gaz. Chim. Ital.	Gazzetta Chimica Italiana.
Gen. Electric Review	General Electric Review.
Glückauf.	
Gummi-Zeit.	Gummi-Zeitung.
Helv. Chim. Acta	Helvetica Chimica Acta.
Indian Trade J.	Indian Trade Journal.
Indiarubber J.	Indiarubber Journal.
Indiarubber World.	
Inst. Chem. Lectures	Institute of Chemistry Lectures.
Inst. Metals	Institute of Metals.
Inst. Min. and Met.	Institution of Mining and Metallurgy.
Intern. Sugar J.	International Sugar Journal.
Iron and Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
Iron and Coal Trades Review.	
J.	Journal of the Society of Chemical Industry.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Inst. Metals	Journal of the American Institute of Metals.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists Association.

J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Chem. Ind. Tokyo	Journal of Chemical Industry, Tokyo.
J. Chem. Met. and Min. Soc. S. Afr.	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Soc.	Journal of the Chemical Society.
J. Dairy Sci.	Journal of Dairy Science.
J. Econ. Entom.	Journal of Economic Entomology.
J. Exp. Med.	Journal of Experimental Medicine.
J. Farmers' Club	Journal of the Farmers' Club.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gasbeleucht.	Journal für Gasbeleuchtung.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. E. E.	Journal of the Institution of Electrical Engineers.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Pet. Tech.	Journal of the Institution of Petroleum Technologists.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Landwirts.	Journal für Landwirtschaft.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. prakt. Chem.	Journal für praktische Chemie.
J. Roentgen Soc.	Journal of the Roentgen Society.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech.	Journal of the Society of Glass Technologists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
J. S. Afr. Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.
J. State Med.	Journal of State Medicine.
J. Textile Inst.	Journal of the Textile Institute.
J. of Urology	Journal of Urology.
Ker. Rundschau	Keramische Rundschau.
Kōgyō-Kwagaku-Zasshi	(Journal of Chemical Industry, Tokyo).
Kolloid Zeits.	Kolloid Zeitschrift.
La. Bulletin	Louisiana Bulletin.
La. Planter	Louisiana Planter.
Lancet.	
Landw. Versuchs Stat.	Die landwirtschäftlichen Versuchs-Stationen.
Leather Trades Review.	
Metall u. Erz	Metall und Erz.
Met. and Chem. Eng.	Metallurgical and Chemical Engineering.
Mitt. K. Materialprüf.	Mitteilungen aus dem Königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und der Hygiene.
Monatschr. Textil Ind.	Monatschrift für Textil-Industrie.
Monatsh. Chem.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monit. Scient.	Moniteur Scientifique.
Muench. mediz. Wochenschr.	Muenchener medizinische Wochenschrift.
Nature.	
New Zealand J. Sci. and Tech.	New Zealand Journal of Science and Technology.
Olien & Vetten.	
Papierfab.	Papierfabrikant.

Papier Zeit.	Papier Zeitung.
Perf. and Essent. Oil Rec.	Perfumery and Essential Oil Record.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentralh.	Pharmazeutische Zentralhalle.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Phot. J.	Photographic Journal.
Phys. Rev.	Physical Review.
Physiol. Abs.	Physiological Abstracts.
Proc. Illinois Gas Assoc.	Proceedings of the Illinois Gas Association.
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenscheppen te Amsterdam. Proceedings (English Edition).
Proc. of M. of S. D. Works	Proceedings of Managers of Sewage Disposal Works.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Tokyo Mathematico-Phys. Soc.	Proceedings of the Tokyo Mathematico-Physical Society.
Purdue Univ. Agric. Exp. Sta.	Purdue University Agricultural Experiment Station.
Rec. Trav. Chim. Pays-Bas	Recueil des Travaux Chimiques des Pays-Bas.
Rev. Agric. et Vétérin. de Madagascar	Revue Agricole et Vétérinaire de Madagascar.
Rev. gén. des Sciences	Revue générale des Sciences.
Rev. Mét.	Revue de Métallurgie.
Schweiz. Chem. Zeit.	Schweizerische Chemiker-Zeitung.
Sci. Abs.	Science Abstracts.
Seifenfab.	Seifenfabrikant.
Sitzungsber. Akad. Wien.	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
Soil Sci.	Soil Science.
South Dakota State Coll. Agric. Bull.	South Dakota State College of Agriculture, Bulletin.
Sprechsaal.	
Statist.	
Sugar.	
The Times.	
Teysmannia.	
Therap. Monatsh.	Therapeutische Monatshefte.
Therapie der Gegenwart.	
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Canadian Min. Inst.	Transactions of the Canadian Mining Institute.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. N. Eng. Inst. Min. Eng.	Transactions of the North of England Institute of Mining Engineers.
U.S. Bureau of Mines, Bull. and Tech. Papers	U.S. Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau of Standards.	
U.S. Comm. Rep.	U.S. Commerce Reports.
U.S. Cons. Rep.	U.S. Consular Reports.
U.S. Geol. Survey	U.S. Geological Survey.
Univ. of Illinois Bull.	University of Illinois Bulletin.

Verhand. geol. Reichsanstalt	Verhandlungen der K. K. geologischen Reichsanstalt in Wien.
Wochenbl. Papierfab.	Wochenblatt für Papierfabrikation.
Woch. Brau.	Wochenschrift für Brauerei.
Z. anal. Chem.	Zeitschrift der analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift der anorganischen Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Z. exp. Path. Pharm.	Zeitschrift für experimentelle Pathologie und Pharmazie.
Z. Farben u. Textil Chem.	Zeitschrift für Farben und Textil Chemie.
Z. f. Instrumentenkunde	Zeitschrift für Instrumentenkunde.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Z. physiol. Chem.	Hoppe Seyler's Zeitschrift für physiologische Chemie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deuts. Ing.	Zeitschrift des Vereins deutscher Ingenieure.
Z. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

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FOODS.

By H. W. Bywaters, D.Sc., Ph.D., F.I.C.,
Chemist, Messrs. J. S. Fry and Sons, Bristol; Lecturer on General Metabolism, Bristol University.

A survey of the literature relating to foods published during the past year reveals a marked influence of the war in several directions. The reduction in our imports from other countries, owing to the submarine warfare, has forced us to devise means for extracting the greatest amount of nutritive substance out of such raw food materials as have been grown or stored in this country. It has led to a great development in the ways of preserving our food, whilst, in order to reduce nutritive material to the smallest possible bulk and weight, and thus facilitate transport, many new methods of concentrating and drying foods have been devised. As the shortness of the supply of the ordinary articles of diet has become felt, we have had to fall back on other hitherto unutilised materials; and methods for preparing foods from acorns, chestnuts, seeds, yeast, &c., have been discovered, and some of them patented. What has happened in Great Britain has occurred to an even greater extent in enemy countries, and extraordinary sources have been tapped for the purpose of obtaining the necessary food wherewith to maintain life in man and beast. These and other similar instances will be found referred to in some detail under the various headings

Flour and Bread.

The primary business of the Food Controller in Great Britain during the last two years has been the conservation of our wheat supplies. It is well known that any excess of moisture in the grain favours the growth of moulds and encourages premature germination, fermentation, and deterioration. Before carefully drying wheat intended for storage purposes, however, the prospect of preserving the grain would be greatly improved if means could be adopted to kill or remove the spores of moulds, bacteria, and other agents, which actually set up the deterioration processes when the circumstances become favourable. As a matter of fact, many proposals have been put forward for treating grain preparatory to storage with the view of enhancing its keeping qualities. Ozonised air,[1] sodium hypochlorite,[2] calcium hypochlorite (calcium hydroxide to neutralise the free acidity of the grain, and a hypochlorite to exert a germicidal action),[3] heat at 60°–70° C.,[4] and other agents, have been suggested; whilst a method has been patented by Frick [5] for improving grain which has become wet or musty, by subjecting it to the action of a mixture of ozone and steam, and then drying in fresh air.

The dilution of wheaten flour with other cereals and substances as a war-time necessity has let loose a flood of communications in which the merits of the various diluents and resulting products have been discussed from the physical, physiological, and economic points of view. The compulsory alteration in the milling of wheat,[6] whereby not less than 81% of the grain was required to be converted into flour instead of the former 70%, caused a revolution in the flour milling industry. At the time of writing it may be taken that as much as 90% of the wheat grain is being converted into flour, which means that some of the branny material of the outer part of the grain, formerly used as cattle food, is now being added, with the germ, to the flour. This alteration affects not only the chemical composition, but also the digestibility and the physiological value of flour. The chief difference in the chemical composition is the increase in fibre and protein arising from the incorporation of the bran and germ respectively, and it is possible that estimations of these two factors alone could be employed for checking the extent to which the milling has been carried.

The subsequent compulsory addition to the 81–90% wheaten flour of from 10 to 25% of another cereal, or other authorised material, to form the ordinary flour for bread-making, has still further altered the composition and the pre-war standard qualities of our chief foodstuff. The practical baker, in choosing which of the possible materials he shall employ with which to dilute his wheaten flour, has probably been guided chiefly by the necessity for producing loaves of the (under the circumstances) best taste and appearance; but scientists have not been backward in their efforts to determine which is really the best adulterant to add, and which will produce the most digestible and physiologically efficient loaf. Many complaints have been raised of the alleged indigestibility of war bread, but on very slender grounds. According to the Report on the Digestibility of Bread, published by the Food (War) Committee of the Royal Society, 1917, numerous experiments on man have shown that breads made up from four parts of 90% wheat flour and one part barley, rice, or maize, are practically as completely digested and absorbed as pre-war bread. These results have been confirmed by Spriggs,[7] and Spriggs and Weir,[8] who report that bread made from a flour containing even as much as one-third of its weight of oatmeal, barley, maize, or rice, is utilised by the human body almost to the same extent as real white bread. The only difference noticeable is that war bread appears to be slightly laxative. These results are not surprising, because wheat bran itself, when ground fine, is digested to a large extent by the body, and, indeed, it has been claimed on this ground that wheat bran should be entirely reserved for human consumption instead of being given to pigs and cattle.[9] Some experiments by Devillers[10] on the digestibility of flours are interesting in this connection. He attempts to replace the rather cumbersome method of experimentation on animals, involving the exercise of continual supervision as well as the analysis of the excreta, by an imitation digestion *in vitro*. He subjects the flour to repeated alternate digestion, first with pancreatin, and then with dilute hydrochloric acid, and regards the insoluble residue finally obtained as equivalent to the portion undigested in the human organism. The results are as follows: wheat grains, 9·9 to 11·5 % of insoluble matter (calculated on the dry substance); flours, 4·8 to 8·2 %; bread, 7·5 %; bran, 35·2 %. Probably experiments *in vivo* would show even greater utilisability of bran. Fedderson[11] finds that when the bran is made into a dough and allowed to remain under suitable conditions, enzymic changes occur which render it more palatable and digestible after its incorporation into bread.

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[1] Moore, Eng. Pat. 116952, *J.*, 1918, 528A.

[2] Von Hagen, U.S. Pat. 1237425, *J.*, 1917, 1145.

[3] Von Hagen, U.S. Pat. 1265700, *J.*, 1918, 528A.

[4] Passburg, U.S. Pat. 1250496, *J.*, 1918, 164A.

[5] Frick and the General Electric Co., U.S. Pat. 1267204, *J.*, 1918, 558A.

[6] Manufacture of Flour and Bread Order (No. 2), 1917; *J.*, 1917, 301.

Digestibility is not the only factor which determines the suitability or otherwise of a material for mixing with flour for bread-making. The value of the starchy matter in a food depends on its digestibility, but the value of the more essential protein element depends on the nature of the protein, on the kind and distribution of its component amino-acids, as well as on the proportion which becomes absorbed. The various cereals have therefore been examined from this point of view, but with somewhat contradictory results. McCollum and Simmonds[12] conclude from their experiments on rats that, provided other necessary dietary constituents are present, the proteins of maize are as efficient as those of wheat for the maintenance of life; whilst the proteins of the oat are of greater value than those of either maize or wheat. This view is also shared by Sherman and Winters,[13] who, in their feeding experiments on a young woman, found that nitrogenous equilibrium was well maintained over long periods on a low protein diet, of which very much the largest part was maize protein. But the experiments of Osborne and his collaborators[14] (also on rats) indicate that neither the proteins from maize nor from oats can effectively replace wheat protein, which confirms the conclusion of Hogan,[15] who found that maize protein was actually deficient in tryptophan and to a less extent in lysine. The proteins of both rice and barley are of high quality,[16] but relatively small in amount;[17] whilst several experimenters ascribe a very high value to the proteins of millet seed.[18]

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[7] *Lancet*, 1918, i. 613.

[8] *Ibid.*, 1917, ii. 724.

[9] Hindhede, *Nederland. Tijds v. Geneesk.*, 1917, 61, 1047; Feer, *Corresp. f. Schweiz. Aertze*, 1917, Dec. 29; from *Physiol. Abstr.*, 1918, 3, 122.

[10] *J. Pharm. Chim.*, 1918, 18, 5; *J.*, 1918, 601A; *Comptes rend.*, 1918, 166, 700; *J.*, 1918, 319A.

[11] Ger. Pat. 303577; *J.*, 1918, 438A.

Most of the materials commonly used with wheat flour for bread-making are lacking in one or more respects when compared to wheat. Maize is deficient in calcium,[19] barley in salts and vitamines,[20] whilst the proteins of millet, although excellent in quality, are not easily digested.[21] I think we may draw the conclusion that a diet consisting principally of one of these cereals is not likely to prove satisfactory; but probably in mixtures of these flours with wheat flour, any physiological deficiency in the former is rectified by the latter.

All these cereals when mixed with wheat flour yield bread which, from the baker's point of view, is of a more or less satisfactory nature. Usually, as most people will have observed, the bread contains more moisture than ordinary pre-war bread.

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[12] *J. Biol. Chem.*, 1917, **32**, 347; *J.*, 1918, 105A.

[13] *J. Biol. Chem.*, 1918, **35**, 301; *J.*, 1918, 601A.

[14] *J. Biol. Chem.*, 1918, **34**, 521; *J.*, 1918, 526A.

[15] *J. Biol. Chem.*, 1917, **29**, 485; *J.*, 1917, 609.

[16] Osborne, &c., *loc. cit.*

[17] Steenbock, Kent, and Gross, *J. Biol. Chem.*, 1918, **35**, 61; *J.*, 1918, 526A.

[18] Langworthy and Holmes, *U.S. Dept. Agric.*, 1917, *Bull.* 525; from *Physiol. Abstr.*, 1918, **3**, 259. McCollum and Simmonds, *loc. cit.*

[19] Hogan, *loc. cit.*

[20] Steenbock, &c., *loc. cit.*

[21] Langworthy and Holmes, *loc. cit.*

Regarding some of the more uncommon materials used in bread it is found that an admixture of 10–15 % of rye or tapioca flour with wheaten flour gives a good loaf,[22] whilst mandioca and soya-bean flour have also been successfully employed.[23] Potatoes—either raw, cooked, or dried—constitute an admirable diluent of wheat flour, and they have been largely employed in Germany.[24] In 1914, at the outbreak of war, there were only six factories in Germany for drying potatoes, but in 1916 these had increased to no fewer than 841, capable of producing twelve million tons of dried potatoes from thirty million tons of raw material. Even this output has been insufficient to meet the requirements of human beings as well as cattle. The desiccation is effected by passage between hot rollers or heating in revolving drums, the former method being capable of dealing with 1·2–1·5 tons of potatoes per hour, and the latter with quantities up to 5 tons per hour. The product, which keeps indefinitely, is sent out in the form of flakes or cubes for cattle, and various flours for human consumption. In this country, until recently, potatoes have been added direct to the dough in the undesiccated condition, because there has been no provision for drying them. Several factories have now been erected, however, both in this country and in America, and it is hoped that potato flour, in various forms, will soon be on the market.[25]

Presentable loaves may be prepared containing up to forty parts of cooked or raw potatoes, freed from peels, per hundred parts of wheat flour.[26] The potatoes should be boiled in their skins, when no appreciable loss of nutrient substances occurs; peeling before boiling leads to a loss of 5% of the total solids.[27] Care should be taken to avoid the use of green, sprouted potatoes, which, owing to their high content of toxic solanines, have been found to cause the death of persons partaking of them.[28]

War-time flour is naturally considerably darker in colour than 70% wheat flour, and various methods have been suggested and patented for conferring a lighter tint on the finished article. Bleaching by a mixture of chlorine and air—the air having been previously saturated with steam and subjected to a disruptive electric discharge[29]—or by hydrogen peroxide,[30] are claimed to improve the colour and baking qualities of the flour. Greville[31] adds small amounts of sulphates or acid sulphates of sodium, potassium or ammonium—either singly or conjointly—to the flour to give greater body and improved pile to the bread. The use of lime-water, which was formerly recommended for removing the inferior taste of bread prepared from dirty wheat, has now been largely discontinued, because the action of the yeast is thereby delayed and the bread is rendered somewhat indigestible, owing to the formation of insoluble calcium triphosphates.[32] To avoid the inhibitory action on the yeast, Le Roy[33] proposes to employ calcium glucosate (prepared by digesting commercial glucose with lime water), which facilitates rather than retards fermentation and is said to give an improved flavour to the bread. Probably a better product is yielded by the method devised by The Ward Baking Co.,[34] in which oxygen or air is pumped into the dough prior to fermentation. It is claimed that a saving of sugar is thereby effected amounting to 1% of the weight of the dough, whilst only 50% of the usual amount of yeast is required for fermentation.

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[22] Balland, *Comptes rend.*, 1917, **164**, 712; *J.*, 1917, 608.

[23] Balland, *Comptes rend.*, 1918, **166**, 846; *J.*, 1918, 387A.

[24] *Bull. Agric. Intell.*, 1916, **7**, 1685; *J.*, 1917, 937.

[25] Compare Condensed Food Co., Eng. Pat. 113900; *J.*, 1918, 256A.

[26] Schaffer, *Mitt. Lebensm. Hyg.*, 1917, **8**, 212; *Physiol. Abstr.*, 1918, **3**, 185.

[27] Weibull, *Kungl. Lanotbrukr. Akad. Handl. Tidskrift*, 1917, **56**, 348; *Physiol. Abstr.*, 1918, **3**, 44.

[28] Harris and Cockburn, *Analyst*, 1918, **43**, 133; *J.*, 1918, 279A.

[29] Alsop, U.S. Pat. 1250072; *J.* 1918, 105A.

The excessive amount of moisture in war bread renders it more susceptible to the growth of moulds, and the larger proportion of the branny part of the grain now left in the flour favours the production of "ropiness," through the action of the *Bacillus mesentericus fuscus* (Flügge)[35] in the bran. The spores of this bacillus are not destroyed during the process of baking; and on subsequent development they form brownish spots in the crumb, whilst a faint sickly odour pervades the loaf. Prolonged baking retards the outbreak of the disease because of its drying effect on the bread, and hence flour suspected of contamination with this bacillus should be treated in this way. Recently several cases of poisoning have been recorded[36] in France which have been traced to flour prepared from a mixture of insufficiently cleaned cereals containing as much as 19% of foreign seeds, including 1·9% of corn-cockle (*Agrostemma githago*). The latter contains a toxic sapotoxin, and it appears possible that contaminations of our war-time flour—similar in character, but to a less degree—may account for the complaints of ill-effects following its use, that have been made from time to time.

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[30] Naamlooze Vennootschap Industrieele Maatschappij, Eng. Pat. 102967; *J.*, 1918, 71A.

[31] Eng. Pat. 117917; *J.*, 1918, 603A.

[32] Effront, *Monit. Scient.*, 1917, 7, 241; *J.*, 1918, 17A. Compare Balland, *Comptes rend.*, 1918, 167, 198; *J.*, 1918, 525A.

[33] *Comptes rend.*, 1917, 165, 416; *J.*, 1917, 1144.

[34] Eng. Pat. 106726, *J.*, 1917, 903.

[35] *J.*, 1917, 697.

[36] Stoecklin, *Ann. Falsif.*, 1917, 10, 561; *J.*, 1918, 163A.

The strength of flour is now generally believed to be dependent upon its gluten constituent, and variations in this respect have been ascribed to the influence of salts and other substances in the grain on the swelling capacity of the gluten.[37] A somewhat different conclusion has been reached by Gortner and Doherty.[38] They have measured the rate of absorption, or loss, of water by weighed discs of moist gluten prepared from different flours and immersed in dilute solutions of various acids, with and without the addition of salts. The results show that the rate of swelling or hydration of the gluten depends largely on the nature of the gluten itself, and not merely on the concentration of the ions in the solution. Gluten from a "weak" flour has a much lower rate of hydration than that from a "strong" flour, and changes from a gel to a sol at a much lower degree of hydration. The authors suggest that the differences between "strong" and "weak" flours are due to intrinsic differences in the glutens which they contain. The difference may be one of size of particles; in "weak" glutens the particles may approach more closely to the boundary-line between the colloidal and the crystalloidal states. In any case, it is evident that a "strong" gluten has the emulsoid properties of a perfect colloidal gel to a much greater extent than a "weak" gluten.

The views expressed above may perhaps be found to harmonise with some practical results recorded in a series of communications by Rousseaux and Sirot.[39] These authors find that the ratio of the soluble to the total nitrogen in a flour may be regarded as an index of its baking value. The most favourable proportion is about 16–17%; if the ratio is higher, due to preponderance of soluble nitrogenous matter, the baking quality is poor, whilst if it is lower, owing to the presence of more insoluble and therefore probably more complex nitrogen compounds, the flour is worked only with great difficulty. The optimum ratio varies with different flours, the values varying from 4·3 for rice to 22·7 for rye.

The analysis of flour, bread, &c., has received some attention during the year, and attempts have been made to establish standard methods of estimation of certain of the constituents. At a conference between the Government Analyst and representatives of the Society of Public Analysts and of biscuit manufacturers,[40] methods for the estimation of moisture and of sugar in biscuits, cakes, buns, &c., were discussed and eventually standard methods were drawn up and agreed to by all parties. An investigation by Birchard[41] on the estimation of moisture in wheat proves that it is impossible to obtain an accurate result by simply drying in an oven or vacuum chamber at a definite temperature to constant weight. A definite loss of weight occurs corresponding to the temperature employed and the length of time of heating; but it is shown that increasing either of these factors leads to a still further loss of weight of the sample. Increase of temperature gives rise to an increased loss in weight that cannot be obtained at any lower temperature, no matter how long the heating be continued. Under these circumstances it is proposed to adopt the Brown-Duval method as the standard method in commercial practice; whilst for those not employing this apparatus, it is pointed out that identical results can be obtained by drying in a Freas electric oven at 100° C. for 54 hours, at 120° for 18 hours, at 130° for 8 hours, or at 160° for 1¾ hours.

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[37] Compare Upson and Calvin, *J. Amer. Chem. Soc.*, 1915, **37**, 1295; *J.*, 1915, 629.

[38] *J. Agric. Res.*, 1918, **13**, 389; *J.*, 1918, 482A.

[39] *Comptes rend.*, 1918, **166**, 190; *Ann. Falsif.*, 1917, **10**, 556; 1918, **11**, 38 *J.*, 1918, 134A, 163A, 279A.

[40] *J.*, 1917, 856.

MILK.

Our knowledge of most of the animal secretions can be regarded still as only of a fragmentary character. Even cow's milk—although it has been the subject of countless investigations—is still a liquid of unlimited possibilities for the research-worker. During the last year, no less than three substances have been detected in it for the first time. Osborne, Mendel, and their collaborators, have commenced a thorough investigation of its composition. They note[42] that besides lactoglobulin, which splits off phosphorus readily, and lactalbumin, which is practically free from phosphorus, a third hitherto undiscovered protein is present which resembles gliadin in being soluble in alcohol.[43] On the other hand, Voegtlin and Sherwin[44] have detected two purines in cow's milk—namely, adenine and guanine—and have actually succeeded in isolating them in a pure state. These facts, although of but little practical value at the present time, may be found later on to possess real importance.

A quick method for the accurate estimation of fat in milk is most desirable; and it is interesting to note that the well-known Gerber centrifugal method, which lays claim to both rapidity and accuracy, continues to yield excellent results when definite conditions are closely observed. Centrifuging for three minutes at 1000 revolutions per minute appears to give most satisfactory figures.[45] The fat may also be calculated, according to Harris,[46] to within 0·1%, and usually within 0·01%, from the specific gravity and the total solids by the addition of two factors, t and s, which are calculated from the formulae $t = \frac{T}{1 \cdot 2} - 8$ and $s = 8 - \left(\frac{G}{4 \cdot 8} + 0 \cdot 116\right)$, where T and G have the same meaning as in Richmond's well-known formula. In the original paper the two factors have been worked out and the results tabulated for all values of sp. gr. from 1·0220 to 1·0370 and of total solids from 10·00 to 13·90, so that all that is required is to determine the respective values, read off the corresponding factors, and add them together to give the fat content of the milk. In a subsequent communication,[47] a formula is given by means of which the percentage of added water in an adulterated milk can be at once calculated from the determined percentages of fat and solids-not-fat in the milk-water mixture.

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[41] *J.*, 1918, 263T.

[42] Osborne, Wakeman, Leavenworth, and Nolan, *J. Biol. Chem.*, 1918, **33**, 7; *J.*, 1918, 134A.

[43] *J. Biol. Chem.*, 1918, **33**, 243; *J.*, 1918, 220A.

[44] *J. Biol. Chem.* 1918, **33**, 145; *J.*, 1918, 134A.

The percentage of fat in milk varies considerably in different breeds of cattle; and, according to the following results,[48] the milk of those breeds of cattle which give the largest volume of milk contains the smallest percentage of fat.

Breed.	Total yearly yield of milk in pounds.	Fat content per cent.
Holsteins	14443	3·44
Ayrshires	9417	3·93
Guernseys	8644	5·03
Jerseys	7491	5·39

It will be observed that although the Guernsey cows gave less milk than the Ayrshires, the absolute amount of milk-fat produced during the year by the former was very much greater.

The removal of fat from milk by skimming can be detected in various ways. Repiton[49] points out that, since for normal fresh milk the ratio of caseinogen to fat is about constant at 0·82, the removal of any of the fat is attended by an increase in this ratio, and any value over unity is a pretty sure indication that skimming has taken place. The percentage of fat in milk is so well known, however, that it is difficult to see what advantage this proposed method has over a simple fat estimation.

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[45] Day and Grimes, *Analyst*, 1918, **43**, 215; *J.*, 1918, 437A.
[46] *Analyst*, 1918, **43**, 263; *J.*, 1918, 437A.
[47] *Analyst*, 1918, **43**, 345; *J.*, 1918, 712A.
[48] Roberts, *J. Agric. Res.*, 1918, **14**, 67; *J.*, 1918, 602A.
[49] *Ann. Chim. Analyt.*, 1918, **23**, 11; *J.*, 1918, 104A.

The value of skim milk is now well recognised in industrial circles, and its uses are many and varied. During this period of food scarcity, there have not been wanting advocates to plead for the entire reservation of skim milk for human consumption The process of curdling such milk and of separating the curds to make fresh cheese is extremely simple, and the nutritive value of the product is high. It has been calculated that in France not less than 35,000 tons of casein would be available from this source alone. Moreover, after the separation of the caseinogen, a similar amount of milk sugar remains in the solution, and by simple evaporation it can be obtained in a dry state ready for storage for months, if necessary. To send such good food material to the pigs or to the glue factory is not economy in war time.[50]

An interesting contribution has been made by Van Slyke and Baker[51] to our knowledge of the process of souring in milk. It has long been known that souring is caused by the lactic acid produced by bacteria. It is now shown that, although the formation of lactic acid commences soon after inoculation with *B. lactis acidi*, it does not become apparent for several hours, because the lactic acid as it is formed is converted into lactate, which is immediately adsorbed by the proteins of the milk. After about twenty hours, the amount of free acid begins to increase rapidly; and when a definite degree of acidity is reached, the milk clots. The first sign of souring in milk is not that afforded by any simple chemical or even physical investigation. Before any other change can be detected, a characteristic flavour appears, discernible to the senses both of taste and smell, and due to the presence of a volatile compound formed in the souring process and not to lactic acid. There does not seem to be any relationship between acidity or hydrogen ion concentration and the appearance of this flavour.

Evidence is slowly accumulating to show that cow's milk, as regards its constituents, is very similar to human milk. Lactose and caseinogen have all their characteristic properties whether obtained from the human, cow, or goat,[52] and probably the same might be said of the fats and other constituents. When cow's milk is to be used for infant feeding, it is most essential that all pathogenic micro-organisms contained in it should be first destroyed, which can be accomplished by pasteurising at a temperature as low as 152° F., but not lower.[53] Even this temperature is sufficient to destroy the vitamines in the milk (see below); and when used for infants, pasteurised milk, like boiled milk, must be supplemented by a material rich in vitamines. The reductase test, in which the milk is heated at 38°–39° C. with a small quantity of methylene blue (1 in 270,000 of milk), affords a ready method for differentiating between good, bad, and indifferent milks. The larger the number of bacteria present, the more rapidly does decolorisation occur.[54] Milk from sick cows may be detected by the low content of lactose (this sugar being attacked early in mammitis), a low refractive index, and a high catalytic activity (catalase from altered leucocytes, bacteria, &c.).[55]

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[50] *J.*, 1918, 321R.

[51] *J. Biol. Chem.*, 1918, 35, 147; *J.*, 1918, 526A.

[52] Bosworth and Giblin, *J. Biol. Chem.*, 1918, 35, 115; *J.*, 1918, 525A.

[53] Vanderleck, *Agric. Gaz. Canada*, 1917, 614; *Physiol. Abstr.*, 1918, 3, 260.

Milk Powder.

It has become increasingly necessary during the war to preserve milk for considerable periods of time and to transport it over long distances. In Germany, preservation has been effected in some cases by freezing the milk.[56] Large refrigerators, holding from 250 to 500 litres, are filled to about one-third of their total capacity with blocks of frozen milk. The remaining space is filled up with sterilised milk at a temperature of 4° C. These refrigerators can then be transported for long distances, the milk remaining in good condition for three or four weeks.

For most purposes, however, before attempting to transport milk, it is desirable to concentrate it, and thereby put it into a condition in which it will keep for a considerable length of time.

The general principle underlying all modern methods for the concentration of milk is that a film of it is heated at a moderately high temperature for a very small interval of time. Under these circumstances, although the material may be transformed into the solid state, sufficient time is not allowed for the coagulation of the proteins to occur. The dry product therefore dissolves fairly readily in water and the solution closely resembles ordinary boiled milk in its appearance and properties. In practice, the two standard methods of concentration applied to milk are well known to be as follows: (1) the milk is allowed to run slowly between a pair of hot rotating cylinders, and the thin film of dried milk formed is then scraped off by a knife; (2) the milk is forced through a fine-spraying nozzle into a dry hot room; the water is rapidly evaporated from each little drop and the residual milk material falls to the bottom of the room as a very fine, dry powder.

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[54] Arup, *Analyst*, 1918, **43**, 20; *J.*, 1918, 69A.

[55] Panchard, *Rev. méd. Suisse romande*; *Schweiz. Apoth. Zeit.*, 1918, **56**, 19; *Physiol. Abstr.*, 1918, **3**, 384.

[56] *J.*, 1918, 366B.

Many patents have been taken out during the last few years for improvements in one or other of these processes, most of which have had for their object the lowering of the temperature to which the milk is heated, or the shortening of the time of exposure to the heat. By very rapid condensation of the moisture given off by the milk, it is possible to produce a considerable vacuum in the hot chamber and thus remove the water from the milk at a comparatively low temperature. The rate of flow of the milk over the heated surface is also increased by replacing the heated cylinder by a hot centrifugal machine. Both of these features are incorporated in a patent of the Merrell-Soule Co.,[57] according to which the milk is run into the bottom of a heated centrifugal chamber, and is made to pass spirally up the side of the chamber by the rotation of a beater at a high speed. The milk is thereby concentrated and passes out at the top, through a fine-spraying nozzle, into a current of heated air, which effects its conversion into a fine powder. The vapour given off in the hot centrifugal passes into a condensing chamber, and its rapid condensation produces a vacuum equivalent to 23–26 inches of mercury in the centrifugal.

Of the many other patents relating to these processes, but one can be here referred to. Its purpose is to reduce the time of heating to a minimum, not by rapid cooling after the heating process, but by endeavouring to keep the milk as cold as possible right up to the moment at which it enters the heated zone. This is effected by the very simple device of circulating cold brine through a jacket surrounding the milk-container and also through the feed-rollers.[58]

Milk powder is an easily digested food with a high dietetic value; but, unfortunately, during the process of manufacture, one essential constituent of a complete food disappears—namely, the vitamines (see later). The anti-scorbutic vitamine in particular, is destroyed, either during the drying process or during the preservation of the dried material, and hence neither infants nor other animals can be maintained for a lengthy period on milk powder, unless some other material rich in anti-scorbutic vitamines is also given from time to time. It is true that it is claimed for some of the patented dried foods that their vitamines are retained, but the indubitable proof of their presence is often lacking. New improvements in the processes of manufacture might lead, of course, to the production of an article more satisfactory in this particular.

[57] Eng. Pat. 111508; *J.*, 1918, 71A.

[58] Butler, Eng. Pat. 117713; *J.*, 1918, 602A.

The purity of milk powders has been the subject of an interesting report to the Local Government Board.[59] Out of eighty-three samples prepared from whole and skim milks, only two were found to be quite free from foreign matter; whilst three contained as much as 0·08, 0·10, and 0·19% respectively of dirt, consisting of sand, sawdust, vegetable fibres, &c. Amongst the impurities found were boric and salicylic acids, sodium bicarbonate and phosphate, calcium oxide, and minute traces of copper. Although the presence of some of these ingredients is indefensible, it is surprising, when one considers the origin and the numerous opportunities for defilement which occur during the preparation of milk powders, that the commercial products possess such a high degree of purity.

Commercial milk powders are also prepared from skim milk, and to these also, since they contain all the proteins of the whole milk, must be assigned a high dietetic value. From some aspects the skim milk preparations have a higher physiological value than those prepared from whole milk, because of the higher percentage of protein in the finished article. The utilisation of skim milk in the production of this dry product should therefore be encouraged.

BUTTER.

A great deal of research work on the composition of butter has been carried out during the past two years, although very little has yet been made public. The results of some investigations by Amberg[60] indicate that, contrary to what is generally stated, the glycerides in butter are nearly all of the mixed type; tributyrin and tricaproin could not be isolated, and even the oleic acid was present for the most part as a mixed glyceride, instead of being in the form of triolein. These results were obtained by hydrogenating the butter fat and separating the constituents of the hydrogenated fat by fractional crystallisation from various solvents. Another method of investigation has been pursued with considerable success by Holland and Buckley,[61] who have esterified butter fat without previous isolation of the saponification products, by boiling the fat with an alcoholic solution of an acid, followed by treatment with ether and an alcoholic solution of magnesium chloride. The mixed esters thus obtained are separated by fractional distillation, and then the percentages of the different fatty acids in butter fat are estimated from the saponification and iodine values of the various fractions. It is, of course, most desirable to obtain a more exact knowledge of the constituents of ordinary butter, particularly from the point of view of the margarine manufacturer, who hopes in the near future to place on the market an article approximating more closely in chemical composition and physical properties to ordinary cow's butter than does the present-day margarine.

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[59] Dobbie, *Food Reports*, No. 24, 1918, 157; *J.*, 1918, 278A.
[60] *Z. Unters. Nahr. Genussm.*, 1918, 35, 313; *J.*, 1918, 558A.
[61] *J. Agric. Res.*, 1918, 12, 719; *J.*, 1918, 346A.

Several methods have been devised for detecting adulterations in butter depending on the varying solubility of different fats in organic solvents. The fatty material is dissolved in a definite solvent and the solution is subjected under definite conditions to cooling or to evaporation until it becomes just turbid. Employing a solution in warm glacial acetic acid, the temperature at which turbidity just occurs is termed the "Valenta number." Stewart[62] recommends absolute alcohol as the solvent, and the turbidity temperature is then termed a modified "Crismer" value. In another modification, the solvent is a mixture of ether and alcohol, and evaporation of the solution is brought about at constant temperature by a rapid current of air until supersaturation is reached and precipitation occurs In this latter method, it is the volume of the solution at the precipitation point which constitutes the desired constant.[63] In each case, the values obtained for the different fats and oils are often very distinctive, and tests on these lines are likely to facilitate the detection of adulteration in butter.

A considerable amount of work has been carried out during the period of the war with the view of ascertaining the best treatment of milk or cream to ensure the greatest keeping quality of the butter prepared from it. Pure fats are very resistant to the attack of fungi, probably because of the lack of nitrogenous and other elements requisite for protoplasmic growth. The fat from the cacao-bean (cacao butter), for example, can be preserved for months without any sign of deterioration, unless contamination has occurred from an outside source.[64] Similarly, spores of moulds in ordinary butter do not germinate or grow; the growth of mould on butter is the result of a contamination from the outside.[65] Cream is more readily attacked, and the moulds secrete enzymes which subsequently produce abnormal flavours in the butter prepared from it. Pasteurisation of mouldy cream destroys the mould, but does not check completely the action of the enzymes, although the keeping quality of the butter is distinctly

[62] *J. State Med.*, 1918, **26**, 312; *J.*, 1918, 668A.

[63] Seidenberg, *J. Ind. Eng. Chem.*, 1918, **10**, 617; *J.*, 1918, 633A.

[64] Compare Batten and Bywaters, *J.*, 1918, 242T.

[65] Combs and Eckles, *J. Dairy Sci.*, 1917, **1**, 347; *J.*, 1918, 668A.

improved. Pasteurisation of cream imparts a marked increased stability to the butter prepared from it, but the best manner in which to carry out the pasteurisation is still a matter of dispute. Whereas some observers [66] hold that prolonged heating at a low temperature (63° C.) is more effectual than rapid (flash) heating at a relatively high one (85° C.), followed by rapid cooling, others [67] maintain exactly the reverse view.

It has been customary to assume that the addition of salt to butter enhances its keeping quality. Investigation [68] has shown, however, that at low temperatures, salt, although preventing the growth of micro-organisms, may actually hasten the deterioration of butter. The precise action of the salt is not clear. It has been noted that at — 15° F. the salted butter loses moisture, whereas the unsalted does not; but this dehydration by salt might have been expected to increase instead of decrease the stability of the butter.

The whole question of the deterioration of butter is a vexed one, especially the cause and nature of rancidity. It is generally believed that rancidity is a condition produced by the growth of micro-organisms; but the actual changes in the composition of the butter thereby produced are still enveloped in mystery. It is usually accompanied by an increase in the acidity, due to the liberation of free fatty acids; but as increased acidity often occurs without any sign of rancidity, there does not seem to be any necessary relationship between them. The micro-organisms responsible for the production of rancidity presumably effect their action through the agency of enzymes, either secreted by or contained in them. Several enzymes can be detected in butter [69]—protease, lipase, peroxidase, catalase; but they are present only in very small amounts and do not seem to play any part in turning the butter rancid. Guthrie [70] draws a similar conclusion from his experiments, in which he finds that the purely chemical and enzymic transformations occurring in butter do not cause rancidity; neither does exposure to high temperatures, light, or air. Although, then, it appears that certain agencies do not cause rancidity, we are not much nearer to the solution of the mystery of its production.

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[66] Hunziker and collaborators, *Purdue Univ. Agric. Exper. Stat.*, Bull. No. 208, 1917, 20, 1; *J.*, 1918, 633A.

[67] Larsen and collaborators, *South Dakota State Coll. Agric.*, Bull. No. 171, Nov. 1916, 529; *J.*, 1918, 526A.

[68] Washburn and Dahlberg, *J. Dairy Sci.*, 1917, 1, 114; *J.*, 1918, 668A.

[69] Thatcher and Dahlberg, *J. Agric. Res.*, 1917, 11, 437; *J.*, 1918, 36A.

[70] *J. Dairy Sci.*, 1917, 1, 218; *J.*, 1918, 526A.

MARGARINE.

The war has rendered much assistance to the development of the margarine industry in this country. Not only has there been a shortage of butter produced in the Homeland, but a reduction—amounting almost to a complete stoppage—of the importation of both butter and margarine from abroad. The average weekly quantity of margarine manufactured in Great Britain has increased from 1611 tons in 1913 to 3564 tons in 1917,[71] but still the demand has exceeded the supply.

An excellent account of the margarine industry, including its growth and position at the end of 1917, was given recently by Clayton.[72] It was pointed out that margarines prepared from a large variety of vegetable oils and fats have been steadily displacing the former purely animal products. Cotton-seed, arachis, soya-bean, sesamé, kapok, maize, wheat, coconut, palm, and palm-kernel oils have all been successfully utilised for the manufacture of margarine. More recently still, hydrogenated oils have been largely introduced, and as these oils seem to possess excellent keeping qualities, the margarine produced from them is also improved in this respect. Objections have been raised against the use of hydrogenated oils on the ground of their alleged content of catalytic agents—such as metallic nickel, or nickel oxide; but physiological tests have demonstrated that quantities of nickel, far surpassing those contained in a daily ration of margarine, produce no ill effects in the human organism, even when administered daily for long periods of time.

Milk is still used in margarine manufacture to assist in the production of the butter flavour and also to bring the added fats into a satisfactory emulsified condition. The milk must be sterilised, either by pasteurisation, or preferably by means of a high-tension alternating electric current, or by exposure to ultra-violet light. It is then inoculated with suitable bacteria and incubated until an agreeable taste is produced, which, however, is not really like the flavour of butter. Apparently, if research can discover the way to reproduce the true butter flavour, water and an emulsifying agent might replace the milk. That this may soon be expected—if it has not already happened—may be gathered from a recent patent[73] granted for an extract of certain seeds or fruits of leguminous plants, which, after fermentation with lactic bacteria, confers a butter-like flavour on an emulsified mixture of edible oils and fats.

For the preparation of satisfactory emulsions, it is necessary to run the oil into the milk and not *vice versâ*; because the emulsion of oil in milk with its colloidal constituents is much more permanent than the emulsion of milk in oil, which would be produced if the second method of procedure were adopted. The addition of 0·1% of glycerin or gelatin to the milk before churning, is stated to lead to much better emulsification and a better quality of the final product.

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[71] Watson, *J. Roy. Soc. Arts*, 1918, **66**, 212; *J.*, 1918, 163A.

[72] *J.*, 1917, 1205.

[73] De Bruyn, Ltd., and De Bruyn, Eng. Pat. 119052; *J.*, 1918, 713A.

The newer type of churn now generally employed is electrically controlled, and is of the "continuous" type—*i.e.*, milk and oils led by separate pipes to a thermo-regulated chamber, where rapidly revolving blades effect complete emulsion. The flow of the milk or oils can be regulated so that various mixtures may be employed as desired. The emulsion is discharged, as soon as it is formed, on to a slanting shoot, where it is met by a spray of cold water, which causes it to break up into yellow granules which, after maturing, are kneaded together to form the butter-like product.

Several new butter substitutes have been patented during the year, most of which consist of vegetable oils incorporated with evaporated skim milk, concentrated whey, or some other fraction or preparation of milk; but scarcely anything of this nature of a really novel or ingenious character seems to have been published.

MEAT, FISH, &c.

Research in the canned goods industries has been carried on in two principal directions. Attempts have been made to determine what are the best means of effectively preserving meats and similar goods in cans and in other ways, and what are the actual changes occurring in the preserved products during storage.

For the effectual sterilisation of meat in small tins, Kossowicz[74] stipulates that the heating should continue at a temperature of 125° C. for at least 45 minutes; if the temperature is raised above 128° by increasing the pressure, the meat becomes too soft and too readily disintegrated. Subsequent rapid cooling (cold shock) does not increase the efficiency of the sterilisation, nor may the heating period be shortened if it is carried out.[75] The preservation of meat may be effected by other means besides boiling, and patents have been taken out recently for an improved method of smoking meat,[76] for preserving in salt and sodium hypochlorite,[77] &c. Attempts have also been made to ensure better preservation by lining the tinned can with celluloid,[78] or with deodorised wood shavings,[79] thus preventing the contained food from coming into contact with the metal.

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[74] *Chem.-Zeit.*, 1917, **41**, 211; *J.*, 1917, 562.

[75] Bushnell, *J. Ind. Eng. Chem.*, 1918, **10**, 432; *J.*, 1918, 482A.

[76] Legg, U.S. Pat. 1250934; *J.*, 1918, 164A.

[77] Rogers, U.S. Pat. 1249205; *J.*, 1918, 71A.

Some interesting observations on the changes taking place in beef during cold storage have been made by Hoagland, McBryde, and Powick.[80] It was found that increases occurred in the acidity, non-coagulable-, amino-, and ammonia-nitrogen, and in the soluble inorganic phosphorus, whilst corresponding decreases were observed in the amounts of coagulable nitrogen and soluble organic phosphorus. These changes are very similar to those occurring when beef is allowed to autolyse under aseptic conditions; and evidently the observed chemical changes may be ascribed to the autolytic enzymes and not to bacterial action. It was noticed that although bacteria and moulds developed on the surface, they did not penetrate the muscular tissue to any great extent. These autolytic changes did not greatly affect the nutritive value of the meat; but the nature of the acids liberated by the hydrolysis of the fats—especially in the kidney and the subcutaneous adipose tissues—rendered the meat in these localities after prolonged storage unfit for human food.

Fish, like meat, may be preserved by boiling and canning, or by keeping in the frozen state. It is essential that fish intended for preservation should be in season. During the spawning season, the fat in the muscular tissues becomes replaced by water, the fat being in part utilised to produce energy and in part transferred to the reproductive organs.[81] Some experiments by Holmes[82] confirm the opinion generally held of the relatively high digestibility of fish: as much as 92% of the protein and 95% of the fat being in some cases digested.

An extraordinary number of patents have been granted during the last few months for apparatus for drying fruits, vegetables, &c. In the majority of cases the drying agent is hot air, which is circulated over the material in trays, or, conversely, the trays are carried on a conveyor through a heated chamber. A rather more novel method for the preservation of fruit syrup is described by Thoms.[83] The apparatus consists of two shallow vessels, clamped together, with a parchment membrane between them. The syrup is placed in one vessel, and water in the other. By rotating or shaking the apparatus, the liquids are made to "glide" over the membrane, and under these

[78] Kahn, U.S. Pat. 1256495; *J.*, 1918, 256A.

[79] Miyauchi, U.S. Pat. 1245489; *J.*, 1918, 38A.

[80] *U.S. Dept. Agric.*, Bull. No. 433, 1917; *J.*, 1917, 936.

[81] Clark and Almy, *J. Biol. Chem.*, 1918, 33, 483.

[82] *U.S. Dept. Agric.*, Bull. No. 649, 1918; *Physiol. Abstr.*, 1918, 3, 382.

Ber., 1918, 51, 42; *J.*, 1918, 190A.

circumstances rapid passage of salts and acids through the membrane occurs, leaving the stabilised fruit syrup with its natural content of enzymes, vitamines, and aromatic flavouring substances. It seems doubtful, however, whether such a method of "gliding dialysis" has any real advantage over a method in which the liquids on both sides of a parchment membrane are maintained in constant circulatory motion, and, also, it does not seem likely that the dialysed syrup will keep for any length of time without further special treatment of one kind or another.

TEA, COCOA, AND COFFEE.

Owing to the scarcity caused by restrictions in the importation of raw materials, there has been a general levelling of the qualities of both tea and cocoa. Thus, in the case of cocoa, practically only the West African cacao-beans have been reaching this country: the beans of higher quality, from Central and South America—the transport of which would mean a longer sea-passage and greater submarine risks—being scarcely obtainable. The division by the Food Controller of the kinds of tea or cocoa into only one or two grades is therefore justified. In the case of cocoa, however, the grounds upon which the distinction between the grades is based have not been happily chosen from the chemist's point of view. Grade "A" and "B" cocoa powders are stated to differ only in their content of admixed cacao-shell—not more than 2% being allowed in the former and 5% in the latter. Now, it is generally recognised amongst chemists[84] that it is impossible to decide by any of the known methods of estimation whether a given cocoa powder contains 2% or 5% of shell. The public must therefore rely solely on the honour of the cocoa manufacturer, who alone is in a position to state exactly how much shell is contained in his products.

A new method for the detection of shell in cocoa powder has been described,[85] which is based on the observation that the ethereal extract of pure cacao-nibs is colourless or only faintly yellow, whilst the extract of the shell is brown. The shells of the different kinds of cacao are treated in such a variety of ways, however, that it seems scarcely possible that any other than a gross adulteration of cocoa powder with shell would be detected with certainty by this method; whilst the proposed test is obviously inadequate for distinguishing between Grade "A" and "B" cocoas.

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[84] Compare Baker and Hulton, *Analyst*, 1918, **43**, 197; *J.*, 1918, 438A.

[85] Keller, *Arch. Pharm.*, 1917, **255**, 405; *J.*, 1918, 37A.

The raw cacao-bean, as it is imported into this country, contains about 12% of shell; and as the cocoa manufacturers use several thousand tons of beans during the year, it might be interesting to know what is being done with the shell. Knapp[86] considers that its proper destination should be cattle food; and although it might be utilised for the extraction of theobromine (which it contains to the extent of about 1%), it should not be used in the adulteration of cocoa or of chocolate, or be sold under a fancy name at a fancy price as a new kind of "tea," affording, when extracted with boiling water, a "refreshing and stimulating beverage"! Several varieties of "cocoa-teas" are now, or have been, on the market,[87] consisting of cacao-shell, containing usually a minute amount of cacao-nib, sometimes mixed with starchy material to give "body" to the drink prepared from it. The greatly inferior stimulating and nutritive value of such "teas," as compared with cocoa, will be apparent from the published analyses.

The flavour of cocoa depends largely on the fermentative treatment the raw bean has undergone before exportation from the Tropics. Any investigation into the changes taking place during this fermentation may therefore be of considerable value. Brill[88] has recently made a study of the changes wrought in the bean through the action of enzymes, and arrives at the conclusion that the time-honoured statement that a glucoside in the bean is hydrolysed during fermentation, with the production of theobromine and cocoa red, is without experimental foundation. The most evident change appears to be the diminution in the astringent matter; and this is brought about by the enzymes in the bean more effectually than by any enzymes added from outside sources—such as yeast enzymes.

The supplies of coffee have been well maintained in this country throughout the period of the war; but in some neutral and enemy countries only substitutes for coffee seem to have been available. The following raw materials are stated[89] to have been consumed in 1916 by six factories in Denmark manufacturing coffee substitutes: Soya-beans, 750 tons; dried chicory-roots, 3411 tons; dried sugar-beets, 654 tons; rye, 706 tons; cacao-shells, 298 tons; maize, 62 tons; dried malt, 23 tons; and oats 16 tons. Lupine-seeds, the seeds of the common corn-spurrey (*Spergula arvensis*, L.), and the so-called acacia (*Robinia pseudacacia*, L.), have also been employed for this purpose in Germany.[90] Lupine-seeds contain alkaloids and saponins, and their use, even after roasting, seems reprehensible.[91] A coffee-like product prepared from the rinds of citrus fruits, by heating first at 180° C. and then at 215° C., has been patented by Bjercke.[92]

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[86] *J.*, 1918, 240T.

[87] Baker and Hulton, *Analyst*, 1918, 43, 189; *J.*, 1918, 437A.

[88] *Philippine J. Sci.*, 1917, 12, A, 1; *J.*, 1917, 1245.

[89] *Chem.-Zeit.*, May 8, 1918; *J.*, 1918, 301R.

[90] Griebel, *Z. Unters. Nahr. Genussm.*, 1918, 35, 233, 272.

New Foods.

The shortage of the ordinary foodstuffs occasioned by war conditions has directed attention to a large variety of materials with the object of preparing new foods to eke out those obtained from pre-war sources. This plethora of new foods has been particularly noticeable in Germany, and is good evidence of the success attending the naval blockade of that country. The most serious danger that could threaten any community is that of the cutting off of its supplies of protein; and to avoid this possibility the Germans early set about, and actually accomplished, what is virtually a synthesis of this invaluable component of the diet, from the nitrogen in the air.[93] The fixation of atmospheric nitrogen is now carried out on a huge scale, affording ample supplies of nitrates for the manufacture of explosives, and large quantities of ammonium salts for synthesising into proteins. The latter transformation is effected by the agency of the growing yeast-cell. A special type of yeast, which multiplies rapidly with the production of a minimum quantity of alcohol, is cultivated in huge tanks, like swimming-baths, containing diluted molasses and other waste sugar from the refineries, together with the ammonium salts. After growth, the pressed yeast is mixed in the fresh or dried state with starchy materials, and then forms, after baking, a palatable food for human consumption. Another method of utilising the yeast is to digest it for some hours with a concentrated sugar solution, which is then evaporated. The resulting syrup contains 2% or more of protein, and resembles malt extract in appearance and flavour.[94]

It is a more difficult problem to remedy the shortage of fats; and although the synthesis of fat occurs in both the animal and the vegetable kingdoms, it does not seem to have been found possible to utilise such a natural process on a sufficiently large scale, or to accelerate it to such an extent as to be able to supply the deficiency of fats in a similar way to that in which the deficiency of proteins has been made good through the agency of the yeast-cell. Elaborate directions for the recovery of fats from household refuse, bones, horse-chestnuts, kernels of cherry-stones, asparagus, and other vegetable seeds, have appeared from time to time; even old and decomposed bones have been utilised for the extraction of fats stated to be suitable for technical purposes.[95] Attention has also been called to the nutritive value of such materials as edible fungi, the horns of cattle, bone marrow, &c.[96] The scarcity of food has been the opportunity for profiteers in other countries besides our own; but the foisting of valueless materials as good food on an ignorant public has been checked in Germany by the operation of the German Food Substitutes Commission, which has laid down, in many cases, the extent to which adulteration or substitution may be carried. Thus it insists that the sale of egg-powders, containing no eggs, shall not be permitted unless the food value is equal to that of eggs; whilst the sale of valueless vegetable preparations purporting to be excellent substitutes for tea is prohibited.[97]

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[91] Gonnermann, *Chem.-Zeit.*, 1917, 42, 296; *J.*, 1918, 483A; Eckenroth, *Z. Unters. Nahr. Genussm.*, 1918, 36, 240; *J.*, 1918, 527A.

[92] U.S. Pat. 1257451; *J.*, 1918, 280A.

[93] *J.*, 1917, 326.

[94] Jalowetz, *Brau- und Malzind.*, 1916, 17, 247; *J.*, 1918, 164A.

The food supply in this country throughout the war has been quite sufficient to maintain the nutritive standard of the population at its normal level. The call for substitutes has not been so great as in other countries; and although certain economies have been effected —such as the greater recovery of flour in the milling of wheat—others have not been rendered necessary. Thus, as has been repeatedly pointed out,[98] the prohibition of brewing would have rendered available considerable supplies of food which have otherwise been largely wasted. The quantities consumed in the brewing industry during the year ending September 30, 1917, were 28,620,800 bushels of malt; 61,200 cwt. of rice; 6200 cwt. of maize, and 1,613,700 cwt. of sugar and its equivalents,[99] and it is calculated that the actual waste occurring in the brewing process was equivalent to the loss of at least 45,000 tons of protein and a total loss of energy such as would have been furnished by 500,000 cwt. of sugar. Some attempts have been made to recover more effectually some of the energy contained in the by-products of the brewery, which have previously been turned to but little account. Processes have been patented for converting spent brewer's or distiller's grains into soluble carbohydrates by acid hydrolysis,[100] or into a diluent for flour, by drying and subsequent milling.[101] The utilisation of brewer's yeast, which accumulates to such a large extent during fermentation, has been for a long time one of the outstanding problems of the brewer's chemist. It has generally been used as a manure or as food for pigs; a small portion is converted into commercial yeast extracts and into some so-called meat extracts. After careful washing to remove the bitter principles, Baker[102] states that it can be mixed with distiller's yeast and used for baking purposes. It may also be liquefied by the addition of salts and converted into dry flaked yeast suitable for human food.[103]

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[95] Kraus, *Chem.-Zeit.*, 1917, **41**, 835; *J.*, 1918, 104A.

[96] See *Physiol. Abstr.*, 1918, **3**, 608.

[97] See further, *Z. anal. Chem.*, 1918, **57**, 170; *J.*, 1918, 437A.

See *J.*, 1917, 198, 279.

J., 1918, 77B.

[100] Ulman, U.S. Pat. 1259568; *J.*, 1918, 317A.

[101] Sleeman, Eng. Pat. 116357; *J.*, 1918, 483A.

Of the food materials which have come into prominence during the war, two deserve special mention—namely, the soya-bean and the cotton-seed. The former, on crushing and pressing, yields an edible oil which can be used in the manufacture of margarine and for a variety of other purposes, whilst the pressed cake, when ground, constitutes an excellent flour, containing as much as 36% of protein, besides fat and carbohydrate.[104] Experiments on animals[105] show that it is readily digested, and contains both the "water-soluble" and "fat-soluble" vitamines. When employed as the sole article of diet, it is found to be deficient in mineral salts but in an ordinary human mixed diet, the salts which are lacking in the soya-bean would probably be abundantly furnished by the other articles in the diet. Cotton-seed[106] also yields an edible oil of excellent quality and a flour with an even higher protein content than that obtained from the soya-bean. Unless carefully treated, cotton-seed meal may be more or less toxic as a cattle food; but during the milling processes it is completely freed from the toxic constituent.[107]

Among other materials which have been suggested for diluting wheaten flour may be mentioned kafir—one of the sorghum grains of America.[108] The kernel has a composition similar to that of maize: the chief protein—kafirin—being deficient in lysine and cystine.[109]

The vegetable kingdom has been ransacked for new food materials to supply real or anticipated deficiencies caused by the war. Among the possible foodstuffs which have been recommended may be mentioned sweet chestnuts,[110] acorns,[111] horse-chestnuts,[112] vegetable ivory,[113] seeds of the silver maple,[114] pigweed-seeds,[115] tomato-seeds [116] (which yield a highly digestible oil and press-cake, resembling the corresponding products from cotton-seed), orange- and lemon-peels and pips,[117] Chinese litchi-nuts,[118] grape-fruit,[119] papaw,[120] and sea-cabbage [121] (*Laminaria digitata*), which can be preserved in the dry state and used for making salad or soup, or turned into a flour suitable for the preparation of biscuits.

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[102] *J.*, 1917, 839.

[103] Petit, *Brasserie et Malterie*, 1917, 7, 257; *J.*, 1918, 163A.

[104] Daniels and Nichols, *J. Biol. Chem.*, 1917, 32, 91; *J.*, 1917, 1286.

[105] Osborne and Mendel, *J. Biol. Chem.*, 1917, 32, 369; *J.*, 1918, 105A.

[106] Vakil, *J.*, 1917, 685; De Segundo, *J.*, 1918, 118T.

[107] Osborne and Mendel, *J. Biol. Chem.*, 1917, 29, 289; *J.*, 1917, 562; Richardson and Green, *J. Biol. Chem.*, 1917, 30, 243; *J.*, 1917, 937.

[108] Bidwell, *U.S. Dept. Agric.*, Bull. No. 634, 1918; *J.*, 1918, 346A.

[109] Hogan, *J. Biol. Chem.*, 1918, 33, 151; *J.*, 1918, 135A.

[110] Baker and Hulton, *Analyst*, 1918, 43, 32; *J.*, 1918, 70A.

[111] Baker and Hulton, *Analyst*, 1917, 42, 351; *J.*, 1917, 1285.

[112] Baker and Hulton, *Analyst*, 1917, 42, 351, and also Goris, *Compt rend.*, 1917, 165, 345; *J.*, 1917, 1107

VITAMINES.

The discovery of these substances in milk by Gowland Hopkins in 1912 [122] has been followed up by numerous researches, particularly in America; but although a considerable advance has been made, the chemical identity of these substances still remains a mystery. The position at the beginning of 1918 is well summarised in the abstract of a lecture by Ramsden,[123] in which it is pointed out that at least three distinct vitamines must be present in the food in order that adequate growth of the person or animal may take place. Attempts are being made in several quarters to separate, isolate, and identify these vitamines. With this purpose in view, Harden and Zilva [124] have studied the differential behaviour which they show towards various adsorbents. The antineuritic vitamine (sometimes termed anti-beriberi or anti-polyneuritic vitamine, or McCollum's "water-soluble B"), which, when included in the diet, prevents beriberi in man and polyneuritis in pigeons, is readily adsorbed by fuller's earth; whilst the antiscorbutic vitamine, which prevents the onset of scurvy in man or in guinea-pigs, is scarcely affected. It is possible, therefore, to remove the antineuritic vitamine almost quantitatively from a solution containing both antineuritic and antiscorbutic vitamines. Dialysed iron and infusorial earth exert a similar adsorptive action on the antineuritic vitamine, and the adsorption compound in the latter case, when given to polyneuritic pigeons, has distinctly active antineuritic properties, which, however, on keeping, slowly vanish.[125] By extracting the "activated" fuller's earth with alkali, Williams and Seidell [126] obtained a crystalline antineuritic substance; but on further purification it lost all its active properties, and was then found to be adenine. Now, pure adenine has been shown by Voegtlin and White,[127] and others, to be quite devoid of antineuritic properties; and one is forced to the conclusion that the antineuritic power of Williams' impure adenine should be ascribed to the impurity and not to the adenine. Williams [128] has published a series of remarkable papers on the chemical structure of the antineuritic vitamine—remarkable, because no one seems to have been able to repeat successfully the experiments he has described. He finds that certain derivatives of the hydroxypyridines can be obtained in two isomeric forms of different stability, of which the more labile one is stated to exert a curative action in polyneuritis. However, until reliable confirmation of his results is obtained, it seems useless to discuss them. A crystalline acid (X-acid), also possessing antineuritic properties, is claimed to have been isolated from aqueous extracts of *Phaseolus radiatus*.[129]

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[113] Chapman, U.S. Pat. 1260327; *J.*, 1918, 347A.

[114] Anderson, *J. Biol. Chem.*, 1918, **34**, 509; *J.*, 1918, 528A.

[115] Harding and Egge, *J. Ind. Eng. Chem.*, 1918, **10**, 529; *J.*, 1918, 528A.

[116] Rabak, *U.S. Dept. Agric.*, Bull. *No.* 632, 1917; *J.*, 1918, 70A.

[117] Mach and Lederle, *Chem.-Zeit.*, 1917, **41**, 830; *J.*, 1918, 105A.

[118] Read, *J. Amer. Chem. Soc.*, 1918, **40**, 817; *J.*, 1918, 387A.

[119] Zoller, *J. Ind. Eng. Chem.*, 1918, **10**, 364; *J.*, 1918, 387A.

[120] Langworthy and Holmes, *J. Home Econ.*, 1917, **9**, 505; *Physiol Abstr.*, 1918, **3**, 259.

[121] Slootzoff and Tschernewski, *Hygiene et Sanitarie*, 1916, Nos. 5 and 6; *Physiol. Abstr.*, 1918, **2**, 608.

[122] *J. Physiol.*, 1912, **44**, 361.

[123] *J.*, 1918, 53T.

[124] *Biochem. J.*, 1918, **12**, 93; *J.*, 1918, 483A.

Of all the sources of antineuritic vitamines, so far discussed, the richest is yeast. Moreover, drying the yeast in the air, or allowing it to undergo autolysis, does not seem to inactivate the vitamine. Some of the commercial yeast extracts possess marked antineuritic power, whilst most meat extracts are valueless in this respect. It is somewhat surprising to find, too, that there are no vitamines in beer, ale, or stout; [130] doubtless the alleged high dietetic or stimulating value of these beverages must be attributed to some other hitherto undiscovered constituents. Extracts of yeast, or small amounts of dried yeast, added to diets which would otherwise induce polyneuritis in pigeons, are quite sufficient to prevent the onset of the disease; and, on the other hand, symptoms of polyneuritis are promptly dispelled on the administration of the yeast.[131] Similar experiments with similar results have also been carried out with cats.[132] The antineuritic vitamine is fairly stable, since it withstands heating for half an hour at 100° C., although it undergoes gradual inactivation at 120° C.[133] These facts concerning the vitamines in yeast encourage the hope that eventually the antineuritic vitamine will be obtained in sufficient quantity from this source to permit of its identification. A possible way of isolation is indicated in an interesting paper by Sugiura,[134] who subjected a strong suspension of dried yeast in 5% sodium chloride solution, contained in a collodion bag, to air-dialysis or percrystallisation.[134a] From 10 grms. of yeast 22 mgrms. of a colourless crystalline substance, almost free from salt, was obtained; and doses of from 2–5 mgrms. dissolved in water and injected subcutaneously into polyneuritic pigeons, abolished all symptoms of the disease in from one to a few hours.

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[125] Bull, *Philippine J. Sci.*, 1917, 12, A, 199; *J.*, 1918, 164A.

[126] *J. Biol. Chem.*, 1916, **26**, 431; *J.*, 1916, 1130.

[127] *J. Pharm. Exp. Ther.*, 1916, **9**, 155; Harden and Zilva, *Biochem. J.*, 1917, **11**, 172; *J.*, 1917, 1063.

[128] *J.*, 1916, 942, 1081, 1130; 1917, 609.

[129] Pol, *J. Physiol.*, 1917, **51**, 432.

[130] Harden and Zilva, *J. Inst. Brew.*, 1918, **24**, 197; *J.*, 1918, 524A.

[131] Emmett and McKim, *J. Biol. Chem.*, 1917, **32**, 409; *J.*, 1918, 105A.

[132] Voegtlin and Lake, *J. Pharm. Exp. Ther.*, 1918, **11**, 167; *Physiol. Abstr.* 1918, **3**, 259.

The rôle which the antineuritic vitamine plays in the organism has not yet been fully established, but it is generally considered that it is in some way concerned with the nutrition of the nervous tissues. Uhlmann [135] finds a close parallelism between the physiological action of the vitamine and that of certain alkaloids, and draws the conclusion that the antineuritic vitamine is a substance physiologically closely related to pilocarpine, which acts on the sympathetic nerve-endings, and exerts a controlling influence over the digestive and metabolic processes through its stimulating action on glands producing internal and external secretions. On the other hand, Dutcher (with Coleatz) [136] has noted a great decrease in the catalytic activity of the tissues in avian polyneuritis; and when the bird is subsequently treated with yeast extracts, the percentage of catalase rises as the symptoms of the neuritis disappear. He considers, therefore, that the antineuritic vitamine regulates the oxidation processes in the tissues, thus preventing the accumulation in the organism of partially oxidised toxic products. It will be very interesting to note the physiological action of the pure substance, when it is obtained.

Accompanying the antineuritic vitamine in yeast, in the outer layers of the grains of most cereals, and in other materials such as butter, a second vitamine is to be found, which has been termed by McCollum "fat-soluble A." Apparently, it is the fat-soluble A which is essential for the promotion of the growth of young animals, although it is unable to exert its action unless sufficient of the antineuritic vitamine is also present. Probably polyneuritis in young pigeons

[133] Drummond, *Biochem J.*, 1917, 11, 255; *J.*, 1918, 134A.

[134] *J. Biol. Chem.*, 1918, 36, 191; *J.*, 1918, 748A.

[134a] Kober, *J. Amer. Chem. Soc.*, 1917, 31, 944; *J.*, 1917, 1038.

[135] *Zeit. Biol.*, 1918, 68, 457; *J.*, 1918, 715A.

[136] *J. Biol. Chem.*, 1918, 36, 63.

could be cured by the administration of the antineuritic vitamine; but further growth would not ensue until an addition of fat-soluble A was also made to the diet.[137] The fat-soluble vitamine occurs in animal fats, but not in fats or oils of vegetable origin; butter or oleomargarines should therefore be given to growing children in preference to margarines prepared entirely from vegetable oils.[138]

A third vitamine is now generally recognised to be responsible for the prevention of scurvy in man and other animals. It occurs in fresh fruit and vegetables, and also in germinating seeds. On heating any of these materials in boiling water, the antiscorbutic vitamine is slowly destroyed; drying the material also appears to remove its activity. Lemon-juice is relatively rich in the antiscorbutic vitamine and seems to be a suitable raw material from which to attempt to prepare, and possibly identify, the active substance. The concomitant citric and other organic acids in the lemon-juice can be removed by calcium carbonate;[139] and on evaporation in a vacuum at 30°–40° C. an active dry residue can be obtained, which has marked protective properties, and when administered to guinea-pigs on an otherwise scorbutic diet effectively prevents the onset of the disease. A curative effect was also observed by Harden and Zilva when the active residue was given in small doses to a scorbutic monkey; but it did not seem to arrest the progress of well-marked scurvy in guinea-pigs. The retention of antiscorbutic power by the juice after the citrates have been removed effectually disposes of the contention of McCollum and Pitz[140] that the curative power of the juice is to be ascribed to the laxative properties of its constituent citrates instead of to a specific vitamine.[141]

Fresh cow's-milk contains the antiscorbutic vitamine, but only to a comparatively slight extent;[142] consequently, any treatment which tends to reduce its meagre content of vitamines renders it inadequate for such a purpose as infant-feeding, unless some other material is supplied containing the missing indispensable substance. Thus if boiled milk, or milk powder, which have been shown to be practically free from the antiscorbutic vitamine, is employed as the sole or principal food for young children, orange, grape, or other fruit juice—or even the raw juice of a swede—should be given from time to time to prevent the appearance of symptoms of infantile scurvy.

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[137] Compare McCollum and Kennedy, *J. Biol. Chem.*, 1916, **24**, 491.

[138] Halliburton and Drummond, *J. Physiol.*, 1917, **51**, 235; *J.*, 1917, 1285.

[139] Harden and Zilva, *Biochem. J.*, 1918, **12**, 259.

J. Biol. Chem., 1917, **31**, 229.

[141] Compare Harden and Zilva, *Biochem. J.*, 1918, **12**, 270.

Chick, Hume, and Skelton, *Biochem. J.*, 1918, **12**, 131.

The immense importance of these accessory substances has been well illustrated by certain observations relating to the health of our troops under various conditions during the war.[143] In December 1915 a number of cases of beriberi occurred among the British troops in Mesopotamia, but practically none among the Indians. This was traced to the fact that the two armies used different flours, and the highly refined British flour was lacking in vitamines, whilst the Indian flour, "atta," containing both the aleuron layer and the germ of the wheat grain, was sufficiently rich in antineuritic vitamine to exert a protective action against the disease. During 1916 a yeast extract, with a high content of antineuritic vitamine, was added to the ration of the British troops, and it is interesting to note that during the following winter, when another outbreak of beriberi might have been expected, very little sign of it occurred. There were only a few very mild cases, and not a single death.

A lack of antiscorbutic vitamines was experienced only by the Indian troops. The Indian has naturally but little reserve against scurvy, and if the supply of antiscorbutic vitamines in the diet is reduced, he readily falls a victim to the disease, whilst the British soldier remains unscathed. In the hot months, when the supplies of fresh food (meat, vegetables, and fruit) were necessarily much reduced, scurvy frequently occurred amongst the Indian troops. The inherent dislike entertained by most Indians for fresh meat was probably one of the factors contributing to the outbreak of the disease. Fresh sour limes and raw potato, converted into a salad with onions and vinegar, were used with much success in combatting the disease. If it had been then known that the antiscorbutic vitamine is formed during the germination of seeds, the scurvy amongst the Indian troops might have been prevented by serving out the peas and beans in their ration in a germinated condition.[144]

CATTLE FOODS.

The war has not been without effect on cattle foods. To obtain the additional percentage of flour from wheat grain prescribed by the Food Controller, a second grinding and sifting of the bran is necessary, and consequently the resulting sharps and bran are relatively poorer in starchy material and more indigestible, as well as being smaller in quantity than in pre-war days.[145] Wheat bran has therefore suffered adulteration with husks of all kinds of cereals, with rice husk, vegetable ivory, sawdust, &c., the presence of which can be most readily detected by means of the microscope.[146] Various processes have been described for increasing the digestibility of straw and other fodders[147] by hydrolytic treatment with soda solution under pressure, and new sources have been drawn upon for materials suitable for incorporation into cattle foods.

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[143] Compare Willcox, *Lancet*, 1917, ii. 677.

[144] Compare Hume, *J.*, 1918, 75B.

[145] Cox, *Analyst*, 1918, 43, 53; *J.*, 1918, 163A.

The necessity for safeguarding as far as possible our supplies of fodder renders it important to discover the cause of the spontaneous combustion of haystacks, which still frequently occurs. It is commonly supposed[148] that, by the action of bacilli in the presence of moisture, a rise in temperature takes place, which leads to the inception of a slow process of dry distillation. This process is accompanied by a still greater rise in temperature and the production of combustible gases and pyrophoric carbon. Eventually a temperature is reached (300°–400° C.) at which spontaneous ignition of the gases occurs. This view has been combatted by Tschirch,[149] who considers that the chief rôle is played not by oxidases, but by reductases, which act energetically between 50° and 70° C. and effect the deoxidation, and eventual carbonisation, of such substances as amino-acids and carbohydrates. Not only is there a production of readily combustible material, but an accumulation of oxygen within the stack; and in the atmosphere thus produced there is great danger of ignition, even when the temperature is comparatively low. Whatever may be the correct explanation, the precautions to be adopted are evident—namely, thorough drying of the hay before stacking (to minimise enzymic and bacterial action) and thorough aeration of the stacks. It has been suggested that the hay should be dried artificially; but this is inadvisable because of the loss of digestibility of the fodder which ensues. As much as 36% of the digestible protein in the original fodder may become converted into indigestible material, even when the drying is conducted at a moderate temperature.[150]

The great strides taken by the oil-seed pressing industry in this country for the purpose of providing fats and oils, and especially the raw materials for the manufacture of margarine, have greatly increased the amount and variety of press-cakes available for cattle food. In this country and in America palm-kernel, coco-nut, ground-nut, and cotton-seed cakes have been largely utilised. The relative digestibility of some of these products varies within small limits,[151] whilst all of them show excellent keeping qualities provided they are stored in a dry place.[152] The use of cotton-seed meal has been called in question on account of the presence in the raw seed of the toxic substance, gossypol. It may be found in all but the woody tissues of the cotton-plant, but it is chiefly concentrated in the seed-kernels. During the cold-pressing process the cells are ruptured, so that commercial "cold-pressed" oil contains about 1·5 % of gossypol.[153] The toxic substance is readily oxidised by atmospheric oxygen at a moderately high temperature and thereby loses its toxicity. "Hot-pressed" oil is therefore free from toxicity, and, after refining, both "hot-" and "cold-" pressed oils may be regarded as harmless. The remaining cotton-seed cake appears to retain slightly the toxic principle,[154] but the injurious action in the cattle food may be lessened or prevented by the addition of iron salts, which appear to facilitate the oxidation of the gossypol.[155]

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[146] Collin, *Ann. Falsif.*, 1917, 10, 539; *J.*, 1918, 163A.

[147] Tollens, *J. Landwirts.*, 1917, 65, 219; *J.*, 1917, 346A.

[148] Compare Jordi, *Schweiz. Chem.-Zeit.*, 1918, 2, 7; *J.*, 1918, 190A.

[149] *Schweiz. Chem.-Zeit.*, 1918, 2, 10; *J.*, 1918, 190A.

[150] Völtz, *Chem.-Zeit.*, 1918, 42, 147; *J.*, 1918, 347A.

The stoppage of the importation of oil seeds into Germany has led to a great shortage of the ordinary pre-war cattle foods in that country, and numerous substitutes have been produced—such as yeast, ground grape-pips, and parsley-seeds[156]—some of which may be expected to obtain a ready market after the war. Of these, perhaps yeast is the most important of the nitrogenous food substances. It is now prepared on a colossal scale in Germany, and has not only been utilised as a food for cattle, but has entered largely into the food of the common people. It is preserved best by drying, although a process for its preservation in the moist state, by further fermentation with lactic acid bacilli,[157] has been put forward. In the dried state, after incorporation with other material, it is readily eaten by animals and almost completely digested.[158] For the supply of carbohydrates, Germany has utilised dried wood pulp, cellulose, molasses, and diseased potatoes.[159] A tasteless product is obtained from the latter, containing about 50% starch and 6% nitrogen, which is stated to have given excellent results in feeding-experiments. Heather, reindeer and Iceland mosses, leaves, and seaweed, have also formed substantial constituents of fodder for horses and cattle. Dried leaves yield quite a valuable "hay,"[160], having a composition and digestibility but little inferior to meadow hay. Heather and the mosses are relatively deficient in proteins,[161] but the use of the former mixed with blood has been advocated, particularly in Denmark.[162] Some kinds of seaweed (*Laminaria*) have been shown to constitute an excellent fodder for cavalry horses.[163] After washing with water, the material contains as much as 17% of proteins and 50% of carbohydrates, and appears to be not much inferior to oats—for which, indeed, it has been substituted with satisfactory results. McHargue[164] has recommended dried insects—such as grasshoppers—as a food for poultry, containing more protein than commercial meat meal.

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[151] Crowther and Woodman, *J. Agric. Sci.*, 1917, 8, 429; *J.*, 1918, 37A.

[152] Godden, *J. Agric. Sci.*, 1917, 8, 419; *J.*, 1918, 37A.

[153] Carruth, *J. Biol. Chem.*, 1917, 32, 87; *J.*, 1917, 1285; *J. Amer. Chem. Soc.*, 1918, 40, 647; *J.*, 1918, 319A.

[154] Withers and Carruth, *J. Agric. Res.*, 1918, 12, 83; *J.*, 1918, 164A.

[155] Withers and Carruth, *J. Biol. Chem.*, 1917, 32, 245; *J.*, 1918, 105A.

[156] *J.*, 1917, 1060; 1918, 76R.

[157] Voltz, *Woch. Brau.*, 1917, 34, 414; *J.*, 1918, 319A.

[58] Crowther and Woodman, *J. Agric. Sci.*, 1917, 8, 448; *J.*, 1918, 37A.

[59] Wehmer, *Chem.-Zeit.*, 1916, 40, 1073; *J.*, 1917, 159.

The effect of cattle foods, of such variety as we have experienced in war-time, on the quality and composition of the milk is a question of interest and importance not merely to the physiologist, but to the farmer, the analyst, and the consumer, because it is now known that alterations in the food of the cow may be accompanied by changes in the taste, the fat content, and general food value of the milk or butter. Thus, feeding with large quantities of cotton-seed cake imparts an oily taste to the butter, and raises its melting-point, whilst improving its keeping qualities.[165] When, however, the ingredients in the food are many and varied, the peculiar effect produced by any one of them on the secreted milk is neutralised and lost. No one seems to have noticed any difference (excepting in price) between war-time and peace-time milks.

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[160] Honcamp, and Blanck, *Landw. Versuchs-Stat.*, 1918, **91**, 291; *J.*, **1918**, 527A.

[161] Honcamp and Blanck, *Landw. Versuchs-Stat.*, 1918, **91**, 223; *J.*, 1918, 527A.

[162] *J.*, 1918, 301B.

[163] Adrian, *Comptes rend.*, 1918, **166**, 54; *J.*, 1918, 70A.

[164] *J. Agric. Res.*, 1917, **10**, 633; *Physiol. Abstr.*, 1918, **3**, 41.

[165] Eckles and Palmer, *Bull. Agric. Intell.*, 1917, **8**, 1021; *J.*, 1917, 1144.

WATER PURIFICATION AND SANITATION.

By Edward Ardern, D.Sc., F.I.C.,
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The continuance of war conditions, with the consequent Treasury restrictions on capital expenditure, has inhibited the activities of Local Authorities upon which material progress in matters relating to this Section is so dependent, and therefore little advance has been made during the period under observation.

On the other hand, military requirements, particularly in America, have necessitated the provision under "hustle" conditions of water supplies for large military camps. It is of interest to note that in the United States[1] sixteen military cantonments, each to accommodate 40,000 troops, were planned and their construction, inclusive of water supply, completed in a little over three months, despite extraordinary difficulties with respect to materials, labour, and transport, at a cost of about £2 6*s.* per head. The total water supply provided was equal to 55 gallons (U.S.A.) per head, which, it is stated, is 80% more than that provided for in English, French, or German camps. Where necessary the water was purified by treatment in sedimentation tanks after coagulation by alum, followed by filtration through gravity filters.

Owing to the shortage of materials, and lack of plant and equipment, the supply of water to troops in the field has called for the exercise of considerable ingenuity on the part of the engineers engaged in this work.[2] The problems have varied from the provision of a more or less permanent supply, *e.g.* base hospitals, cantonments, &c., to a portable or mobile water supply to troops actually in the field. The treatment of the water has varied according to the source of supply. In some cases artesian wells have yielded adequate supplies of potable water of such purity that no treatment was required. On the other hand, where it has been necessary to employ river water, in some cases the turbidity has been such that coagulation with precipitants and preliminary sedimentation prior to filtration and final chlorination has been called for, while in many cases it has been possible to dispense with preliminary coagulation and in others direct chlorination has been sufficient to produce a satisfactory water. One type of mobile purification plant[3] consisted of a three-ton motor wagon equipped with a petrol-driven pump, having a capacity of 1200 gallons per hour, against a pressure of 100 lb. per sq. in., with provision for applying chlorine gas at the pump suction and with delivery (after addition of alum) to a mechanical pressure filter. To ensure absolute safety, relatively large quantities of chlorine have been used (4·5 to 10 parts per million), and provision made for dechlorination by means of thiosulphate, after a contact of from ten to fifteen minutes. A by-pass is provided so that filtration may be omitted when permissible, and the output correspondingly increased. In the forward portion of the truck a well-equipped water-testing laboratory is provided. A lighter type of mobile purification plant of double the above capacity has also been employed, equipped only for chlorination. On these plants the admission of chlorine is controlled by the Wallace-Tiernan[4] apparatus, which has proved so successful in operation that it is being extensively employed in the chlorination of public water supplies. This apparatus is supplied in two types, (*a*) direct feed and (*b*) solution feed, both of which are modified according to whether the chlorine is to be applied to water supplies in open conduit or in pipes under pressure. The chlorination of practically the whole of the Greater New York water supply is controlled by this particular machine. At the Dunwoodie Station alone a volume of 340 million gallons (U.S.A.) per day is chlorinated by means of a range of Wallace-Tiernan apparata. This is easily the largest chlorination plant in the world.

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[1] D. H. Maury, *Eng. News Record,* 1918, 80, 33; J. M. Goodell, *ibid.,* 80, 35.

[2] R. K. Tomlin, *ibid.,* 1918, 81, 434 and 458; Anon., *ibid.,* 1918 81, 670.

The continued high *per capita* water consumption in the majority of American cities is causing serious concern, and in many cases investigations are being made with respect to the possible economy that may be effected. Such an investigation in relation to the city of Chicago[5] has revealed the fact that at least 60% of the total consumption is lost by leakage. General meterage of the supply is recommended, whereby it is anticipated the consumption will be reduced from 295 to 125 gallons (U.S.A.) *per capita* per day. Inasmuch as 2,500,000 people are supplied with water pumped from Lake Michigan, it is obvious that this would mean a considerable saving in pumping and treatment costs. Treatment of the water is at present confined to chlorination, although filtration is anticipated in the future. The opening of a new water-pumping station in Chicago[6] in August 1918 has afforded opportunity for improving on existing stations, particularly in eliminating delicate parts, joints, and valves, and in giving a more dependable distribution of the desired amount of chlorine. In view of the rapidly increasing use of chlorine for the sterilisation of water supplies, it may be of interest to describe briefly the chlorination apparatus employed (wet feed type) which it is stated has been developed by the Municipal Supply Co., Chicago, from sensitive flour-bleaching apparatus. The plant treats 110 million gallons (U.S.A.) per day, and its capacity will be ultimately 152 million gallons. Two independent sets are installed in case of breakdown. The unit consists of a battery of nine chlorine cylinders connected to a common receiver for equalisation of pressure, from which the chlorine passes to an "aerisostat," a pressure-reducing device of special design obviating the use of spring-controlled diaphragm valves, which proved a frequent cause of breakdown in the older types of apparatus. It consists of a closed vessel divided into two unequal parts by a fixed diaphragm passing almost to the bottom. A vertical pipe connects the smaller (outlet) division with a float chamber, the float spindle passing down the pipe, and by means of levers, actuating a valve in the inlet division which cuts off the supply of chlorine, when the float rises to a predetermined point. The closed vessel contains concentrated sulphuric acid (to keep the liquid chlorine dry) sufficient to support the float and immerse the lower edge of the diaphragm, a gauge glass and outlet tap being provided for the exact regulation of the quantity. The admission of chlorine (accurately controlled by a special needle valve) forces the acid into the float chamber, raising the float and closing the cut-off valve until the fall of pressure allows the float to fall, again opening the cut-off valve. After this reduction of pressure, the chlorine passes upward through mixing towers (7 feet high, 8 inches diam.) filled with pumice-stone, meeting a stream of filtered water sprayed in at the top. The resulting solution of chlorine is then introduced into the main body of water at a point on the rising main some distance below the pumps. The "aerisostat" and mixing towers are installed in a heated and fan-ventilated chamber, the temperature of which is controlled by a thermostat. Incidentally it is stated that the number of samples per thousand showing *B. coli* present in 1 c.c. is reduced by chlorination from 18 to 0·9, and this treatment of the water supply is believed to have effected a reduction of 70% in the death-rate due to typhoid fever.

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[3] *Eng. News Record*, 1918, **81**, 458.

[4] Eng. Pats. 113105, 113106, 113198, 113288, 113374; *J.*, 1918, 191A, 192A.

[5] *Eng. News Record*, 1918, **80**, 269.

While bleaching powder is rapidly being replaced by liquid chlorine in the sterilisation of public water supplies, there are cases where it can be employed to advantage, especially in emergency, and moreover hypochlorites are extensively employed in surgical work. Attention is therefore drawn to the important investigation of Rettie[7] and others with respect to the prevention of loss of available chlorine on storage of bleaching powder, particularly in warm climates. Their results demonstrate that by the admixture of freshly ignited quick lime, 20% in excess of the quantity required to combine with the moisture present, the loss of available chlorine after storage under typical tropical conditions is very strikingly reduced, as also is the formation of calcium chlorate which accompanies the decomposition. The latter observation is of special interest in connection with the use of bleaching powder under tropical conditions for water sterilisation, in view of the serious effect upon the palatability of the water of the addition of more than a minimum quantity of chlorate.

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[6] J. Ericson, Amer. P. H. Ass., Dec. 1918; *Eng. News Record*, 1918, **81**, 1126.

The permutit process of water treatment has been found peculiarly adaptable to war requirements and has been applied extensively to the softening of water used for cooling purposes in aeroplane engines, or for gas or other internal combustion types of engines, and laundry work, &c.

A novel method of water softening has been patented by E. Edser[8] and others in which tri- or di-sodium phosphate and caustic soda are employed. The precipitated calcium and magnesium salts are produced as a froth by the addition of sodium oleate and violent agitation with air. Iron salts are also removed from solution. The use of baryta in place of soda for softening water is revived by F. Hundeshagen.[9] A. S. Behrman[10] has examined the Blacher[11] method for the determination of hardness in water and recommends the following modification. If the free carbon dioxide exceed 25 parts per million, the water is aspirated for ten minutes prior to determining the temporary hardness by titration with $\frac{N}{10}$ sulphuric acid, using dimethylaminoazobenzene as indicator. A slight excess of $\frac{N}{10}$ acid is here added, air aspirated through the solution for five minutes, and 1 c.c. of phenolphthalein (1%) added, followed by $\frac{N}{10}$ alcoholic caustic potash until a slight pink colour is noticed. Titration at this stage with $\frac{N}{10}$ potassium palmitate until an intense pink is obtained gives the total hardness. The same author has also adapted this method for field purposes.[12]

The position with respect to rivers pollution has suffered very severely as the direct result of war conditions, especially so in certain industrial centres, where there has been a set-back of at least ten years.

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[7] T. Rettie, J. Lorrain Smith, and J. Ritchie; *J.*, 1918, 311T.

[8] Eng. Pat. 118668; *J.*, 1918, 670A.

[9] *Z. öffentl. Chem.*, 1918, 24, 159, 175, 186; *J.*, 1918, 670A, 713A.

[10] *Philippine J. Sci.*, 1916, 11, A, 291; *J.*, 1918, 19A.

[11] *J.*, 1913, 158.

[12] *Philippine J. Sci.*, 1918, 13, A, 27; *J.*, 1918, 348A.

The principal factors contributing to this state of affairs are:

1. Lowered efficiency of existing sewage purification plant by reason of serious labour shortage and difficulty in executing repairs and renewals, with consequent reduction in effective capacity and deterioration in character of effluent obtained.
2. Inability to proceed with new works and consequent failure to cope with increased flow of sewage.
3. Enormous expansion of the chemical industry with special reference to the production of explosives, with more or less corresponding increase in polluting and in many cases inhibitory waste liquors, which has added to the difficulty already referred to in regard to the efficient operation of sewage purification plants.
4. In special cases the effective treatment of trade waste discharged into water-courses has been interfered with by lack of the necessary reagents.

While trouble due to factors 3 and 4 may readily be overcome, it is obvious that some considerable time must elapse before the deficiencies in sewage purification plants generally are repaired and the works brought up to even the pre-war standard.

Fortunately some compensation for this state of affairs is found in the fact that, despite all the difficulties of the general situation, progress has been made with the development of the activated sludge process as a practical and economic means of sewage purification, especially as in the opinion of the writer this process is destined to play a great part in the future development of the problem of sewage disposal.

Great interest continues to be evinced in this process by those responsible for the treatment of sewage, and investigations have been continued in this country, Canada, Australia,[13] and the United States. The progress made during the period under observation may be briefly summarised as follows:

The working scale continuous flow unit[14] installed at the Withington Sewage Works (Manchester), mentioned in last year's report, has been in operation for a period of fifteen months and has given results in advance of those anticipated. This plant, which was designed to treat 250,000 gallons of sewage per day with an average aeration period of four hours, has proved capable of caring for at least 375,000 gallons per day with the production of a satisfactory effluent. Operating at this rate the aeration period is about three hours. Studies with respect to the minimum air consumption, which have included the use of a pulsating air supply, indicate that with a weak domestic sewage of the character of that treated at the above works, it need not exceed 1·0 cubic foot of free air (compressed to 3½ lb.) per gallon of sewage treated. In view of the fears originally entertained with respect to the blockage of the air diffusers, it is important to note that up to the present no trouble has been experienced in this direction and the friction of the diffusers has not increased appreciably after fifteen months' operation. In this connection, tribute should be paid to Messrs. Jones & Attwood, Ltd., who have supplied the whole of the equipment of not only this plant but of all similar installations in this country, and to whose enterprise is due to a large extent the progress made in the working scale development of the process, especially as the firm has been mainly responsible also for the design of such plant. Experience with this plant has demonstrated that fluctuating flows due to varying rainfall can be accommodated fairly readily, provided of course that due provision is made for adequate settlement of the sludge prior to discharge of the purified effluent. The writer has been favourably impressed with the efficiency of the inlet arrangement for feeding the final settlement tank which was designed by W. Clifford (Wolverhampton), as the result of an extended study of the principles involved in the correct design of upward flow tanks of the type employed in this installation.

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[13] A. Cronin, *Austral. Pharm. Notes*, 1917, 18–20; *J.*, 1918, 106A.

[14] Ardern, *J.*, 1917, 822. *Annual Report for year ending March* 1918, *Rivers Department, Manchester Corporation.*

In view of the satisfactory results obtained from this plant and from a " fill and draw " activated sludge tank which has treated the city sewage at the rate of 45,000 gallons per day for the past twelve months, the Rivers Committee of the Manchester Corporation decided to extend their investigations at their Main Outfall Works at Davyhulme, where a strong trade sewage from an industrial population of nearly 800,000 people is dealt with. The construction of a continuous flow plant designed to treat 1,000,000 gallons of screened and detritus-free sewage per day is now well advanced. While the general layout of this installation is similar to that at the Withington Works, the depth of the aeration chamber is increased from 6 to 9 feet, and an entirely different arrangement of the diffusers has been adopted with a very considerably reduced ratio of diffuser area to total tank area. Whereas in the Withington plant the diffusers (four, each 1 foot square over all) are placed in the furrows of a ridge-and-furrow concrete floor, transversely to the direction of the flow of sewage, in the new plant narrow diffusers (7 inches wide) are to be employed arranged parallel to the central axes of the aeration channels alongside the divisional walls which have a curved footing, while numerous cross-baffle walls are provided to obviate any short-circuiting that might result from the spiral motion induced by the admission of air through the diffusers.

The whole object of this new design, which was developed by Messrs. Jones & Attwood, Ltd., from their investigation of the currents induced by the admission, under varying conditions, of air into water, is to enable a flat-bottomed tank to be employed and at the same time obviate the deposition of sludge on the floor of the tank, which would become de-aerated and liable to disturb the efficiency of the process. If successful this type of tank will mark a considerable advance in design, inasmuch as the construction is simplified and the cost per unit capacity appreciably less than that of the type previously employed.

The activated sludge plant at the Worcester Sewage Works, which is capable of treating 750,000 gallons of sludge per day, remains in operation, and the question of extending the process to the treatment of the whole flow of sewage is under consideration.

During the year an experimental plant has been operated at St. Albans,[15] which has demonstrated that the process can be applied successfully to the purification of the St. Albans sewage; doubtless the information afforded by this plant will be helpful in regard to future extensions of the existing purification plant.

The results are awaited with interest of the operation of a continuous flow unit which has been recently brought into commission by Makepeace at Tunstall, inasmuch as the design of the aeration chamber offers a variant from that of the Withington and Davyhulme plants alluded to previously. The ratio of diffuser area to tank area lies midway between that of these two installations. The diffusers are arranged transversely to the direction of the flow of sewage, but the construction of the floor of the tanks is such that the concrete ridges occupy less space than in the Withington plant. Cross-baffles, with central orifice, are provided in front of each line of diffusers, so that the admission of air will induce a circulatory motion in each of the compartments between the cross baffle walls.

The publication of the original paper by E. Ardern and W. T. Lockett[16] relating to the activated sludge process aroused considerable interest in America and the process was at once studied at several centres. As the result of two years' experience with a working-scale continuous-flow unit, Chalkley Hatton was so favourably impressed with the process that he prepared a scheme[17] to treat the whole D.W.F of the Milwaukee sewage, amounting to 85,000,000 gallons (U.S.A.) and storm water up to 235,000,000 gallons (U.S.A.) per day. This scheme has been postponed, however, mainly owing to the increased cost due to war conditions, the difficulty of obtaining the necessary labour, and also the fact that the data with respect to certain questions of design were considered insufficient to justify extensions on so large a scale. The demonstration plant has been remodelled therefore with the view of obtaining further information in relation to the best proportion of diffuser area to tank area, the proper depth of aeration chamber, and the most efficient type of settlement tank, and also with regard to other matters of minor importance. In a recent communication (Jan. 1919) to the writer Mr. Hatton states that information of value has been already obtained with respect to these questions. It may be observed that while the present American research is tending towards an increase in the diffuser area, in this country the aim is to reduce as far as possible the ratio of diffuser area to tank area, and therefore it should be helpful to compare eventually results obtained from the remodelled Milwaukee plant with those yielded by the latest English installations. In considering this important factor in design it must be remembered that the function of the air is twofold—aeration and admixture of sewage and sludge. Considered purely from the point of view of efficiency of aeration, *i.e.* air solution, obviously the greater the proportion of diffuser area the better; but unfortunately this means increased equipment cost, and if the air consumption is not increased, low air velocities through the diffusers with consequent greater likelihood of unequal distribution and trouble due to partial blockage of the tiles. While the aeration efficiency (actually due to air admission) will certainly suffer by a reduction in the diffuser area, the circulatory action of the air will be increased if proper attention is paid to the design of the aeration chamber, which means a much greater exposure to the atmosphere of sewage and sludge by continual surface interchange, and judging by Haworth's studies, referred to later, sufficient attention has not hitherto been paid to this aspect of the problem, so far as its effect on the maintenance of aërobic conditions is concerned.

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[15] A. Eade, Assoc. M. of S. D. Works, 1918.

[16] *J.*, 1914, 523.

[17] *Milwaukee Sewerage Commission, Fourth Annual Report,* **Jan. 1918.**

The writer is informed (November 1918) by Mr. E. E. Sands, City Engineer, Houston, Tex., that for some time past the continuous-flow activated sludge plant installed at Houston has treated 10,000,000 gallons (U.S.A.) per day, with the production of a well-clarified effluent. No trouble has been experienced with the operation of this plant, and the average air consumption amounts to 1·0 cubic foot free air per U.S.A. gallon of sewage treated.

The chief condition to fulfil in the design of working-scale plant is to maintain the activated sludge in complete suspension, *i.e.* in intimate contact with the sewage under aërobic conditions. In the whole of the installations previously mentioned, the agency employed for this purpose has been compressed air, admitted through diffusers; it is therefore important to observe that Haworth[18] has made material progress in the development of his earlier studies, in which mechanical means are employed both for keeping the sludge in suspension and for air induction. Recently the small-scale experiments have been translated to larger outdoor plant. Two tanks, each of 10,000 gallons' capacity, have been constructed, which it is estimated should be capable of treating 60,000 gallons of sewage per day. The tanks, which are each 30 feet long, are divided by longitudinal walls so as to form a channel 120 feet long by 3 feet wide. The plant is operated on the "fill and draw" system, and the sewage and sludge during treatment is circulated through the channel by a specially designed mechanical device which is operated at such a speed as to produce a linear velocity of approx. 2 feet per second, which prevents deposition of the sludge. In addition, air is induced mechanically in the manner employed in the earlier experimental work. After a period of from four to five hours' circulation the contents of the tank are allowed to remain quiescent and the purified effluent is withdrawn. The outstanding feature of this plant is that apparently aërobic conditions are maintained, chiefly by the constant exposure to the atmosphere of a rapidly changing surface of the mixture of sewage and sludge. The design of this plant is much simpler than that of the continuous-flow units already mentioned, and its equipment cost should be materially less. On the other hand, as at present operated, it suffers from the known disadvantages of a "fill and draw" system and it would appear difficult to translate on to a continuous-flow system, as effective and repeated circulation of the whole of the sewage is an essential feature of this method of operating the process. As the final consideration is one of cost (capital and maintenance) in relation to efficiency, it is fortunate that this plant is on sufficiently large a scale to enable reliable data to be obtained with respect to operation charge, which can then be compared with the known cost of working scale activated sludge plants already in operation.

The leading features of the activated sludge process are: (1) Concentration of area of purification plant; (2) freedom from nuisance; (3) high clarity and low bacterial content of purified effluent; and (4) recovery in the resultant sludge of a high proportion of the original nitrogen content of the sewage treated. In connection with the remarkably high percentage removal of bacteria effected by the activated sludge process, reference may be made to an interesting comparison instituted by W. R. Copeland,[19] Chief Chemist to the Milwaukee Sewerage Commission, in which he gives the bacteria (grown at 20° C.) removal effected by the various methods of sewage disposal investigated as follows: Imhoff tank, 12% removal; 8 ft. sprinkling filter, 49%; chemical filtration, 36%; activated sludge, 90–95% removal. He states further that the cost of chlorinating Imhoff tank effluent (7 parts Cl per million) so as to equal the bacterial removal effected by the activated sludge process, is greater (Milwaukee conditions) than that of the air required for the activated sludge process. He concludes, therefore, that from the standpoint of removal of bacteria alone (apart from any other consideration), the continuous-flow activated sludge process is cheaper than Imhoff tank treatment followed by chlorination.

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[18] *Proc. of M. of S. D. Works*, 1917.

[19] *Milwaukee Sewerage Commission, Fourth Annual Report*, Jan. 1911.

In the opinion of the writer the outstanding feature of the process is the recovery in the sludge of a large proportion of the organic nitrogen present originally in the sewage treated, in a form peculiarly suitable for agricultural purposes. Its value as a fertiliser has been already investigated by Bartow and Hatfield,[20] Nasmyth and McKay,[21] and others, and it is satisfactory to note that the Government are sufficiently interested in this aspect of the problem to call for a special report on the subject. In connection with this official investigation, which it is understood will include a study of the source and character of the nitrogen present in the sludge, a special demonstration plant is now under construction. The question of the most economical method of dewatering and drying the sludge so that full advantage may be taken of its manurial value is therefore of paramount importance. A considerable amount of work on this problem has been already done. Chalkley Hatton,[22] as the result of a fairly extensive investigation concludes that by preliminary dewatering in a special type of sludge press, with subsequent treatment in a rotary cylindrical direct-heated dryer, a product containing not more than 15% of water can be obtained at a considerably less cost than the value of the resultant dried material. Authoritative information with respect to this method of treatment should soon be available as the result of the operation of a large scale dewatering and drying plant which, according to a communication received from Mr. E. E. Sands, should now be in commission at Houston, Texas. Probably on account of its gelatinous condition, activated sludge is not so readily dewatered as ordinary sewage sludge, and the correct solution of this problem involves in the first place a study of the conditions influencing the elimination of water retained by colloids in the "gel" condition. The question is at present being studied at the Withington Sewage Works (Manchester), where it is proposed to compare the efficiency of centrifugal action with the results obtained from the ordinary sludge press, with and without preliminary treatment of the sludge. Preliminary treatment of the sludge will include acidification, application of heat, and electrification. The writer is not without hope that the latter agency will prove helpful in the direction of rupturing the gelatinous envelope of the colloid "gels" and thus assist in the elimination of water. Once the water content has been reduced to about 70%, no difficulty need be anticipated in the subsequent drying of the sludge down to a marketable product by treatment in any one of several mechanical dryers on the market whose efficiency has been demonstrated in many industrial operations.

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[20] *J. Ind. Eng. Chem.*, 1916, **8**, 17; *J.*, 1916, 552.

[21] *J. Ind. Eng. Chem.*, 1918, **10**, 339; *J.*, 1918, 384A.

[22] *Some Conclusions reached concerning the Treatment of Sewage by the Activated Sludge Process*, Sept. 1917.

It will be seen from the foregoing that, although the practical nature of the activated sludge process has been established, there is still a fairly wide field for research in relation to improvements in plant design and with respect to the best means of preliminary dewatering of the resultant sludge.

War conditions have stimulated progress with respect to the utilisation of garbage, particularly in the United States, and attention is drawn to a paper by M. N. Baker,[23] in which data accumulated by the United States Food Administration is ably summarised. Quite a considerable proportion of American cities are feeding garbage to hogs or reclaiming from it fats and fertiliser by means of "reduction." Some attention has been paid in the United States to the Miles acid process of sewage disposal,[24] which involves the treatment of the sewage with sulphur dioxide gas, with the production, after sedimentation, of a sterile effluent comparatively free from suspended matter, and subsequent recovery (by extraction) of grease from the resultant sludge. Winslow and Mohlman[25] report favourably on this process in connection with the treatment of New Haven sewage, which it is stated contains inhibitory trade waste (copper salts) in sufficient quantity to interfere with the biological treatment of the sewage, *e.g.* Imhoff tanks or activated sludge process. It should be noted that the conditions at the point of discharge do not demand a highly oxidised effluent, provided elimination of sewage bacteria and suspended solids is accomplished, and moreover war conditions are favourable to the application of the process, as its success, even with this standard in view, is to a large extent conditioned by the price obtained for the recovered grease. Average English conditions require the oxidation of the organic matters in solution, and consequently the process is unlikely to find application in this country, except perhaps in the preliminary treatment of certain industrial sewages where in some cases acid precipitation has been employed for some years past.

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[23] *Eng. News Record,* 1918, **81,** 715.

[24] *Ibid.,* 1918, **81,** 1034; *Met. and Chem. Eng.,* 1918, **18,** 591: *J.,* 1918 439A.

[25] *Eng. News Record,* 1919, **82,** 32.

Interest has been revived also in this country, mainly as the result of war conditions, in the idea of recovering grease from sewage, and in this connection reference may be made to extraction plant[26] in operation under the direction of Mr. J. H. Garner[27] at the Huddersfield Sewage Works, which during the past year or two has proved highly remunerative by reason of high prevailing price of fats, &c. The sludge removed from the sewage by sedimentation is acidified in the cold (preferably with sulphuric acid, although nitre-cake has been employed) and dewatered from 92% to 45% by preliminary treatment in the usual plate sludge press. The pressed cake after disintegration is dried in a Ruggles-Coles mechanical rotary cylindrical dryer. The resultant product, with water content of about 15%, is extracted by solvent (benzine, b.pt. 100°–120° C.) and the recovered grease refined (freed from dirt and water) by treatment with steam and acid. While recognising that the financial results obtained from the plant during recent years are entirely abnormal by reason of the inflated price of fats, the treatment of sewage from the centres of the woollen industry even in normal times presents a special problem, and will do so as long as certain manufacturers continue to discharge to the sewers suds containing such a proportion of soap, &c., as is at present the case.

The problem of the recovery of valuable products from sewage is not only highly interesting to those concerned with the question of sewage disposal, but is one of very considerable importance from the point of view of national economy. Obviously nitrogen and grease are the two main products which are capable of utilisation. The activated sludge process offers better prospects of success in the recovery of a high proportion of nitrogen, in a form available for agricultural purposes, than does any other known process, but the adoption of this method of sewage treatment leads to a considerable loss of greasy matter, probably as the result of lipolytic enzyme action, and the grease content of the resultant sludge is so low as to render its recovery impracticable. On the other hand, the nitrogen content of the degreased sludge resulting from present-day methods of grease recovery is not only much less than that of activated sludge but it is doubtful whether it is in a form so readily available for plant nutrition

Whether, in cases where the grease content of a sewage is sufficiently high to justify its recovery, the problem will resolve itself into a separate preliminary treatment (acid precipitation) for grease recovery, followed by purification by the activated sludge process with recovery of nitrogen in the sludge, or whether means will be devised whereby the major portion of the grease can be separated mechanically without precipitation, so that full advantage may be taken of the activated sludge process and the production of two types of sludge avoided, is a question for the future to decide. In any case, the writer believes that the amount of grease at present removed from the surface of the sewage could be appreciably increased by the provision of suitably designed grease traps, prior to the main treatment of the sewage.

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[26] J. H. Garner and J. F. Carmichael, *J. Soc. Dyers and Col.*, 1918, **34**, 113; *J.*, 1918, 430A.

Annual Meeting, Assoc. Man. of S. D. Works, London, Dec. 1918.

The whole question of sewage disposal, involving as it does the purity of water-courses and conservancy of waste products, is so obviously a national one, that it is highly desirable that effect should be given to the recommendation of the Royal Commission on Sewage Disposal with respect to the formation of a Central Authority with power to deal with all aspects of the problem, with especial reference to the conduc of research.

FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS.

By George Barger, M.A., D.Sc.,
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This review has been arranged on a similar plan to that of the two previous reports. Naturally some of the subjects there dealt with are not now represented, and other new ones have been introduced. The work of 1918, of rather slender volume, has not been dealt with exhaustively; on the other hand several subjects not previously included, have been traced back through a number of years. As the war is drawing to a close, little need now be said of its effect on industry. The progress recently made in this country is to some extent reflected in the Descriptive Catalogue[1] of the British Scientific Products Exhibition, held from August 12 to September 7, 1918. This catalogue contains a number of special articles on different branches of chemical industry, including one on drugs and fine chemicals by C. A. Hill. Some information may also be gleaned from the list of exhibits. Much has been done during the war, much more remains to be done during peace.

Commercial Syntheses of the Simpler Aliphatic Compounds.

As this subject was fully dealt with in the two previous reports we need now only consider the work of the current year.

Chlorinated hydrocarbons may be produced by mixing chlorine and natural gas in a body of charcoal at low temperature and then passing them through a body of charcoal at 300° C.[2] The cost of making chloroform from alcohol by Besson's process (successive treatment with chlorine, bleaching powder, and milk of lime) has been investigated by K. Ukita,[3] who finds that it compares very favourably with the acetone process. A new modification of the preparation of carbon tetrachloride from carbon bisulphide and chlorine forms the subject of two patents.[4]

Published by the British Science Guild, 199 Piccadilly, London, W. 1.

J. B. Garner and H. D. Clayton, U.S. Pat. 1262769; *J.*, 1918, 349A.

J. Chem. Ind. Tokyo, 1918, 21, 219; *J.*, 1918, 442A.

G. Baillio, U.S. Pats. 1260621 and 1260622; *J.*, 1918, 349A.

Use of calcium carbide.[5]—In Switzerland the annual production of calcium carbide is stated to have increased from 4000 tons (in 1901) to 90,000 tons[6] and the manufacture of ethyl alcohol from it is in progress, so that this country will be able to export alcohol, instead of importing it as hitherto.[6a] G. Foth[7] has given a computation against the use of carbide for the production of alcohol and argues (possibly *pro domo*) for the retention of the fermentation process, as follows: one ton of carbide yields 625 litres of alcohol, which quantity is also obtainable from 125 cwt. of potatoes; one ton of carbide will, however, yield 1250 kilos of nitrolim containing 250 kilos of nitrogen, and since manuring with 1 kilo of assimilable nitrogen may increase the yield of potatoes by as much as 100 kilos, the ton of carbide, converted into nitrolim, would yield an extra 25 tons of potatoes, and by fermentation 2500 litres of alcohol, or four times the quantity obtainable by the other method; in addition the residual liquor after distillation is available as fodder. The production of alcohol from calcium carbide, as well as from other sources, has been discussed in several appendices to the new German bill for creating an imperial alcohol monopoly.[8] It is stated that the annual production of nitrolim in Germany will be 500,000–600,000 tons, but whether any of the carbide is diverted for the manufacture of alcohol will depend on the relative facility with which other nitrogenous fertilisers will be obtainable, *e.g.* by the Haber process. Another appendix to this bill refers to the production of alcohol from spent sulphite liquors of the wood pulp industry. These contain 1% of sugar and yield after fermentation about 5·8–6·7 litres of alcohol per cubic metre of liquor. Since 1909 alcohol has been manufactured in Sweden by this process, and during the war also in Germany. The product contains a little methyl alcohol.

Whatever doubt may exist as to the advisability of converting carbide into alcohol, there is none with regard to the production of acetaldehyde and acetic acid. The hydration of acetylene to acetaldehyde[8a] by using mercury compounds and an acid bath continues to be the subject of patents[9, 10], and in the second of those quoted, a yield corresponding to 90–95% of the theoretical is claimed. A quite different method of hydration consists in passing acetylene, freed from phosphorus compounds and mixed with steam, over hot oxides, *e.g.*, molybdic oxide. The catalyst is regenerated and freed from catalytic poisons by strongly heating it in a current of air.[11] As regards the aerial oxidation of acetaldehyde to acetic acid, the best catalyst is stated to be copper at 150°–200° C.; chromium compounds are also said to be very efficient.[12] Ethylidene diacetate, produced from acetylene and acetic acid, *e.g.* in the presence of methylene sulphate,[13] may be decomposed almost quantitatively into acetic anhydride and paraldehyde by heating in a vacuum with an acid catalyst (2% sulphuric acid at 70°–80°/100 mm.).[14] The acetaldehyde obtained from acetylene is mainly either oxidised to acetic acid or reduced to alcohol, but it may be put to other uses. By means of strontium oxide it may be converted into aldol,[15] and P. Sabatier and G. Gaudion[16] describe its "crotonisation" by passing it over thorium, titanium, or uranium oxide at 300° C. The products of this reaction may be passed over reduced nickel, and then furnish mainly a mixture of normal butyl and hexyl alcohols.

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[5] For a general account see *Chem. Trade J.*, 1918, 283.

[6] *Chem.-Zeit.*, 1918, **42**, 395.

[6a] In 1912 Switzerland produced 30,000 tons of carbide, of which 26,000 tons was exported, nearly all to Germany. By 1917 the production had more than doubled, and in the first quarter of 1918 the export to France was 7,500 tons, *i.e.* at a greater rate than six years ago to Germany. (*Zeit. angew. Chem.*, 1918, **31**, III., 469.)

[7] *Z. Spiritus-Ind.*, 1918, **41**, 162; *Chem. Zentr.*, 1918, ii. 214.

[8] *Chem.-Zeit.*, 1918, **42**, 311.

[8a] For a discussion of the priority of early patents see *Zeit. angew. Chem.*, 1918, **31**, 148 and 180.

[9] H. Hibbert, U.S. Pat. 1247270; *J.*, 1918, 74A.

[10] H. Dreyfus, Eng. Pat. 105064; *J.*, 1918, 222A.

A somewhat novel reaction of calcium carbide has been described by C. Davidson.[17] By adding this substance, free from iron, to a saturated solution of chlorine in benzene, tolane di- and tetra-chlorides, $C_6H_5.CCl:CCl.C_6H_5$ and $C_6H_5.CCl_2.CCl_2.C_6H_5$, are obtained. Attempts to make sodium acetylide react with aldehydes and ketones, after the manner of sodium phenylacetylide, have, on the other hand, met with little success; most of the substance is decomposed to acetylene, which escapes without reacting.[18]

Alcohols, glycols, and their derivatives.—A detailed study of the decomposition of ethyl alcohol into ethylene and water, or into acetaldehyde and hydrogen, by various catalysts between 380° and 500° C. has been made by C. J. Engelder.[19] By passing alcohol vapour over soda lime B. H. Carroll[20] brings about the reaction

$$C_2H_5OH + NaOH = CH_3CO_2Na + 2H_2.$$

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[11] E. F. Scheller, U.S. Pats. 1244901 and 1244902; *J.*, 1918, 20A.

[12] H. Dreyfus, Eng. Pat. 108459; *J.*, 1918, 266A.

[13] Soc. Chim. des Usines du Rhône, Eng. Pat. 112766; *J.*, 1918, 606A.

[14] Soc. Chim. des Usines du Rhône, Eng. Pat. 110906; *J.*, 1918, 282A; compare Eng. Pat. 23190 of 1914; *J.*, 1915, 982.

[15] N. Grünstein, U.S. Pat., 1234156 and Eng. Pat. 101636 *J.*, 1917, 1064.

[16] *Comptes rend.*, 1918, 166, 632; *J.*, 1918, 322A.

[17] *J. Amer. Chem. Soc.*, 1918, 40, 397; *J.* 1918, 202A.

[18] K. Hess and H. Munderlich, *Ber.*, 1918, 51, 377.

[19] *J. Phys. Chem.*, 1917, 21, 676; *J.*, 1918, 19A.

[20] *J. Phys. Chem.*, 1918, 22, 128; *J.*, 1918, 281A.

This change, which begins at 250°, is followed by the decomposition of the sodium acetate into methane and sodium carbonate, and this decomposition attains at 450° almost the same rate as the formation of sodium acetate. Aldehyde tars, ethylene, and water are formed in small amounts, but apart from this the main reaction at 450° is therefore the decomposition of alcohol into methane, carbon dioxide, and hydrogen.

Various patents deal with the production of a mixture of ethylene-, propylene-, and butylene-glycols[21] from natural oil gas and chlorinated hydrocarbons (see above) and with the production of chlorohydrins[22] from the same source.

The pentane fraction of petroleum can likewise be chlorinated and the monochloropentane, after fractionation, be converted into amyl acetate. A calculation of the cost of this process has been made by B. T. Brooks, D. F. Smith, and H. Essex.[23] The synthetic ester cannot be distinguished from ordinary amyl acetate as regards its solvent power for cellulose esters, &c.

Chlorinated hydrocarbons may also be used for the production of ethers, if they are passed, mixed with the unchanged hydrocarbon, over a basic oxide, such as lime, at 250°–450°; thus for the preparation of ethyl ether, chlorine and three volumes of ethane are made to react at 300°–550°, and after removal of hydrogen chloride, the mixture of ethyl chloride and ethane is submitted to the action of lime.[24]

Preparation of aldehydes.—The reduction of acids to aldehydes is attended with considerable difficulty. Frequently the esters have been employed, but now K. W. Rosenmund[25] seems to have found an excellent method in the catalytic reduction of the acid chlorides by means of palladinised barium sulphate containing 5% of metal, or by Kelber's nickel catalyst.[26] The acid chloride is dissolved in three to five volumes of dry xylene or cumene and the solution is boiled while hydrogen is bubbled in; hydrogen chloride escapes. The acid chloride may even contain traces of phosphoryl chloride. This remarkable application of catalytic reduction often gives very high yields (benzaldehyde, 97%; butyraldehyde, 50%).

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[21] P. McElroy, U.S. Pats. 1259757 and 1259758; *J.*, 1918, 283A. H. Hibbert U.S. Pat. 1270759; *J.*, 1918, 531 A.

[22] K. P. McElroy, U.S. Pat. 1253616; *J.*, 1918, 167A.

[23] *J. Ind. Eng. Chem.*, 1918, 10, 511; *J.*, 1918, 530A; see *Ann. Rept.*, 1917, 471.

[24] B. S. Lacy, U.S. Pat. 1245742; *J.*, 1918, 20A.

[25] *Ber.*, 1918, 51, 585; *J.*, 1918, 441A.

[26] C. Kelber, *Ber.*, 1916, 49, 55; 1917, 50, 305; *J.*, 1916, 382, 1130.

SACCHARIN.

The most important development in the production of fine chemicals in this country during the last year has been the manufacture, on a large scale and by economically sound methods, of saccharin. Before the war only the last stage of the synthesis was carried out here, from imported *o*-toluenesulphonamide. Now, saccharin is manufactured by five firms, with a yearly output capacity more than equal to the total annual consumption before the war. The saccharin so produced has been controlled by the Ministry of Food through their hold on toluene and oleum, and a selling price was fixed which left a large margin of profit for the State, the proportion allowed to the manufacturer being only of the order of 3*s*. to 4*s*. per pound.

Notwithstanding the large output which was attained, the demand was so far in excess of the supply that the saccharin imported into this country from foreign sources, the price of which was left uncontrolled, realised such high prices, that the profit gained by the traders reached as high a figure as 167*s*. per lb. above that allowed to the British manufacturer. This has enabled them to write off the cost of their plant, &c., and put them consequently in a relatively better position for future competition.

Another respect in which the foreign manufacturer is favoured is that his manufacturing work is unhampered by Customs control and restrictions.

A comparison of the qualities of British and foreign saccharin tablets may, in some respects, afford satisfaction to the British producer; it certainly does not to the consumer, often unable to obtain controlled saccharin. The latter is not allowed to be issued if it contains less than 95% of benzoylsulphonimide, and H. D. Richmond[27] has found that the average is 97·6%, which is somewhat higher than the 550-saccharin imported before the war (most of the pre-war import was, however, 330-saccharin). H. D. Richmond, S. Royce, and C. A. Hill[28] have recently examined a large number of controlled and uncontrolled tablets (from British and foreign saccharin respectively). Whereas 40% of the 200 controlled samples made by various firms conformed to the official requirements, and the remainder nearly all showed a deficiency of much less than 10%, the 160 samples of uncontrolled tablets examined were very much inferior. Thirteen were full strength, fourteen showed a 10% deficiency, and more than half were deficient to the extent of 50–70%. Prices have little connection with strength;

[27] *Analyst*, 1918, **43**, 349.
[28] *Ibid.*, 1918, **43**, 402; *J.*, 1919, 55A.

the most expensive were often also among the weakest. Frequently a definite claim of full strength is fraudulently made, and it would appear that there is here scope for the application of the Food and Drugs Act to put an end to such practices.

With regard to analytical methods reference may be made to a paper by H. D. Richmond and C. A. Hill.[29] The various reactions involved in the production of saccharin can here only be alluded to. The sulphonation of toluene is now generally carried out by means of chlorosulphonic acid.[30] The chief problem is the separation of the *o*- and *p*-isomerides formed (the *m*-isomeride only occurs in minute amount).[31] A partial separation may be effected by freezing out the *p*-toluene sulphonic chloride.[32] The amides may be further separated by fractional crystallisation of their alkali salts[33] and by fractional precipitation of the amides by acids, when the *o*-isomeride separates first.[34] Magnesium and ammonium salts such as the chlorides have also been suggested for the purpose;[35] the former precipitate the magnesium salt of the ortho-amide, the latter the ortho-amide itself. The oxidation of the *o*-amide to saccharin has been carried out by means of permanganates of potassium, sodium, and calcium, or electrolytically, and may be carried out with advantage below 60° and in the presence of excess of amide. The solution should be neutral or slightly alkaline.[36] The final purification of saccharin may be carried out in various ways, *e.g.* by fractional conversion into alkali salts.[37] The latter process applied to commercial saccharin containing 40% of *p*-sulphaminobenzoic acid resulted in the introduction of "550-saccharin" into commerce.

The estimation of *o*- and *p*-toluene sulphonic acids in a mixture of the two has been carried out by A. F. Holleman and P. Caland[38] by means of the freezing point curve of the acid chlorides, but in a recent paper P. V. McKie[39] has given a similar curve for the amides, which are preferable for this purpose and show a sharply defined eutectic point.

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[29] *J.*, 1918, 37, 246T.

[30] P. Monnet, Eng. Pats. 25273 (1894) and 9962 (1899).

[31] A. F. Holleman and P. Caland, *Ber.*, 1911, **44**, 2504.

[32] Majert and Ebers, Eng. Pat. 6581 (1897).

[33] Chemische Fabrik von Heyden, Eng. Pats. 6198 and 22726 (1894).

[34] *Ibid.*

[35] Barge and Givaudan, Eng. Pat. 848 (1903).

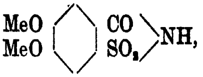
[36] *Ibid.*, Eng. Pat. 3563 (1903).

[37] C. Fahlberg, Eng. Pat. 22787 (1891).

[38] Ber., 1911, **44**, 2504.

[39] *Chem. Soc. Trans.*, 1918, **113**, 799; *J.*, 1918, 684A.

The sweet taste of saccharin is not possessed by closely related derivatives, *e.g.* not by veratric sulphinide,



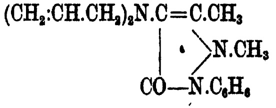
which J. F. McG. Brown and R. Robinson[40] have synthesised, nor by selenosaccharin, prepared by R. Lesser and R. Weiss,[41] in which selenium replaces sulphur. (For the chemistry of sweet flavours see *Nature*, Jan. 23, 1919, 412.)

ANTIPYRETICS.

Salicylic acid.—A method of purification has been patented[42] which consists in blowing a current of dry air into the melted acid at 170° C., the latter being kept thoroughly stirred. Crystals of salicylic acid are deposited in a series of condensers, say at 130°, 95°, and 40°, and the last traces are held back by a filter. Volatile impurities like phenol remain in the air without being deposited. The acetylation of methyl salicylate to the methyl ester of acetylsalicylic acid[43] and the preparation of acetylaminophenyl salicylate (salophen)[44] have been described.

Phenacetine analogues.—Acyl derivatives of *p*-aminophenol allyl ether[45] are stated to possess narcotic, sedative, and anti-neuralgic properties. The acetyl derivative is fairly soluble in water and melts at 94°. The lactyl-, the α-bromo-isovaleryl, and the isovaleryl compounds[46] have also been protected.

Pyramidone derivatives.—Pyramidone (4-dimethylamino-antipyrine) is soluble in 18 parts of water, but by adding an equivalent of ethylurethane a preparation is obtained soluble in an equal weight of water and suitable for subcutaneous injection.[47] Phenacetine analogues were mentioned above in which the ethyl group is replaced by allyl; the allyl group has also been introduced (by the same firm) into the antipyrine molecule, to form a pyramidone analogue, 1-phenyl-2.3-dimethyl-4-diallylamino-5-pyrazolone.[48] This substance,



$$\begin{array}{l}(CH_2{:}CH.CH_2)_2N.C{=}C.CH_3\\ \qquad\qquad\qquad\quad | \quad \rangle N.CH_3\\ \qquad\qquad\qquad CO{-}N.C_6H_5\end{array}$$

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[40] *Chem. Soc. Trans.*, 1917, 111, 952; *J.*, 1917, 698.

[41] *Ber.*, 1912, 45, 1835.

[42] M. Theodor, Eng. Pat. 115080; *J.*, 1918, 349A.

[43] L. Thorp, U.S. Pat. 1255950; *J.*, 1918, 223A.

[44] R. Q. Brewster, *J. Amer. Chem. Soc.*, 1918, 40, 1136; *J.*, 1918, 580A.

[45] Ges. für chem. Ind. in Basel, U.S. Pat. 1263238; *J.*, 1918, 349A.

[46] Ges. für chem. Ind. in Basel, Eng. Pat. 116920; *J.*, 1918, 531A.

[47] Farbw. vorm. Meister, Lucius und Brüning, Ger. Pat. 305369; *J.*, 1918, 443A.

[48] Ges. für chem. Ind. in Basel, Ger. Pat. 304983; *J.*, 1918, 389A.

is stated to have a stronger and more prolonged antipyretic action than pyramidone without being more toxic; in addition it has a marked narcotic effect not possessed by the latter substance.

ANTISEPTICS.

In last year's report [49] mention was made of the controversy as to the most suitable bacteriological test for antiseptics, of which the war has produced a considerable number. It is becoming more and more recognised that different organisms may vary considerably in their sensitiveness to any particular antiseptic, and it follows that in some infections one substance is the best, while in other infections a quite different antiseptic may be preferable. Examples of this specificity are given in a recent book by C. H. Browning.[50] Thus brilliant green is more destructive to coliform bacilli than to *B. typhosus*; thallium acetate suppresses *B. pyocyaneus* and organisms of the proteus type, while allowing streptococci to grow. *B. diphtheriæ* is considerably more resistant to telluric acid than the majority of pathogenic organisms, and thorium nitrate has a discriminating action in favour of *B. mallei*. These various substances may be therefore employed, alone and in conjunction with one another, to facilitate the isolation of an organism by enrichment methods.

Dihydroquinine homologues.—Other and very striking examples of specificity, which have been studied quantitatively, have recently been brought to light among the homologues of dihydroquinine, the alkyl ethers of dihydrocupreine. The first of these, ethyldihydrocupreine or "optoquin," [51] was shown by Morgenroth to have a specific action on *Pneumococcus*,[52] but as the base is poisonous and may produce blindness, its clinical application in pneumonia has not been very successful; its use has been prohibited in the German army.

More recently propyl-, butyl-, *iso*-amyl-, hexyl-, heptyl-, *iso*-octyl-, decyl-, duodecyl-, and cetyl-dihydrocupreines have been prepared and examined. Their preparation is effected by reducing the vinyl group in quinine,[51] and demethylating the resulting dihydroquinine to dihydrocupreine. The latter is then converted into an *o*-alkyl derivative by an alkyl halide. The bacteriological examination has shown that whereas pneumococci are most readily destroyed by the ethyl ether, vibrios, *e.g.* *V. choleræ*, are most sensitive to the *iso*-amyl compound,

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[49] *Ann. Repts.*, 1917, 478.

[50] *Applied Bacteriology.* Henry Frowde and Hodder & Stoughton, London, 1918.

[51] *Ann. Repts.*, 1916, 286.

[52] For summary of literature to the end of 1914 see J. Morgenroth, *Berl. klin. Wochenschr.*, 1914, No. 47/48.

"eucupin," and most other pathogenic organisms, such as *B. diphtheriæ*, streptococci, staphylococci, to the *iso*-octyl derivative, "vuzin."[53] The latter has attracted considerable attention in Germany as a wound antiseptic (*iso*-octyl alcohol is readily obtained from castor-oil). Vuzin, which is the dihydrochloride, is employed in very dilute solution (*e.g.* 1 : 10,000). The relative antiseptic power measured by *Staphylococcus* is as follows: quinine and ethyldihydrocupreine, 1; *iso*-propyldihydrocupreine, 2; *iso*-butyldihydrocupreine, 8; *iso*-amyl- and hexyl-dihydrocupreine, 10–12; heptyl- and *iso*-octyl-dihydrocupreine, 40: but as has been pointed out, other organisms may give different results. The "toxines" with an *iso*-amyl and with an *iso*-octyl group (corresponding to quinotoxine) are more active than the parent bases.[54]

The *hypochlorite preparations* suggested by H. D. Dakin and by J. Lorrain Smith were discussed last year[55]; a general account by T. Rettie[56] has also appeared. The manufacture of chloramine-T has been described by J. K. H. Inglis[57] and an improved method for preparing Dakin's dichloramine-T (toluene-*p*-sulphodichloro-amide, $CH_3.C_6H_4.SO_2.NCl_2$) on a large scale has been given by R. B. Krauss and E. Crede.[58] This substance may be used as a spray, if it is dissolved in some solvent which it does not attack. As such chlorinated eucalyptol has been employed,[58] but H. D. Dakin and E. K. Dunham[59] consider chlorinated paraffin wax ("chlorcosane") to be the best solvent. *Trypaflavin* (= *Acriflavine*)[60] has now also come into use in Germany as an antiseptic. M. Flesch[61] has employed it successfully in the treatment of gas gangrene, and Baer and Klein[62] report favourably on its effect in gonorrhœa.[62a] The former author refers to an explanatory leaflet issued by the makers (Cassella & Co.) giving directions for washing out the stains of this antiseptic. According to A. Abelmann[63] dilute (0·1 %) solutions of flavine are decomposed by light, with the formation of a brown deposit; more concentrated solutions (1%) keep much better. Attempts have been made to combine the disinfectant action of acridine dyes with that of the heavy metals, by making silver and mercury compounds of 2.7-dimethyl-3.6-diaminoacridinium chloride.[64] A silver compound of methylene blue ("argochrom") has been recommended for intravenous injection in puerperal fever and general infections.[65]

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[53] J. Morgenroth und Tugendreich, *Biochem. Zeit.*, 1917, **79**, 257. H. Schæffer, *Biochem. Zeit.*, 1917, **83**, 269; *J.*, 1918, 191A. R. Bieling, *Biochem. Zeit.*, 1918, **85**, 188; *J.*, 1918, 221A.

[54] J. Morgenroth und E. Bumke, *Deut. medizin. Wochenschr.*, 1918, **44**, 729.

[55] *Ann. Rept.*, 1917, 475.

[56] J., 1918, 23T.

[57] *J.*, 1918, 288T.

[58] *J. Amer. Chem. Soc.*, 1917, **39**, 2720; *J.*, 1918, 72A.

[59] *Brit. Med. J.*, Jan. 12, 1918; *J.*, 1918, 135A.

[60] *Ann. Rept.*, 1918, 477.

[61] *Muench. mediz. Wochenschr.*, 1918, **65**, 970.

[62] *Ibid.*, 1918, **65**, 970.

[62a] Similar observations on its use in gonorrhœa were made simultaneously by E. G. Davis and B. E. Harrell, *J. of Urology*, 1918, **2**, 299.

[63] *Pharm. Zeit.*, 1918, **63**, 270; *J.*, 1918, 559A.

Various.—*ar*-Tetrahydronaphthols and their derivatives, substituted in the aromatic nucleus by nitro or alkyl groups, halogens, or mercury salt residues, are said to possess a disinfectant power greatly in excess of that of the parent substance.[66]

"Ixolon," a zinc salicylate containing boron, is a white crystalline powder, fairly readily soluble in warm water. It is stated to be very useful in the treatment of gonorrhœa,[67] and is described as "diborozinc tetra-*o*-hydroxybenzoic acid"; according to a German medical paper[68] this "shameful" circumlocution for a salicylate imposes on the chemical ignorance of physicians. The preparation is a copy of "zibosal" or zinc "borylsalicylate," used for the same purpose.[69] Borodisalicylic acid, $HO.B:(OC_6H_4COOH)_2$, is the subject of a patent,[70] and has been recommended as an internal antiseptic.

A further German preparation for use in gonorrhœa is "choleval," made in tablets containing 10% of colloidal silver. The protective colloid is, however, not a protein decomposition product, as in other silver preparations of the same type, but sodium cholate. The theoretical basis for this deserves some attention. It has been known for some years that certain cocci, *e.g. Pneumococci*, are dissolved by bile salts. Mair has shown that sodium desoxycholate is ten times as active as sodium cholate; he has also given a simple method for preparing desoxycholic acid from bile.[71] H. Wieland and H. Sorge,[72] in an interesting paper, have shown that desoxycholic acid has the power of forming molecular compounds with a large number of substances, which dissolve in water as sodium salts. So that the action of choleval is in reality due to desoxycholic acid, which not only keeps the silver in suspension but also increases the penetration of the disinfectant. Wieland and Sorge showed that desoxycholic acid may contain acetic acid of crystallisation in equimolecular proportions, forming a compound of the same type, but its power of addition is not limited to complexes with fatty acids. It will combine with such diverse substances as benzene, naphthalene, azobenzene, colophony, strychnine, and quinine, which complexes are all more or less soluble in water as sodium salts. This property may well find further application in bringing otherwise insoluble drugs into a water-soluble form, particularly in the alkaline intestinal contents. These addition compounds have been protected,[73] especially that with phenol.

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[64] Ges. für chem. Ind. in Basel, U.S. Pat. 1227624 and 1259517; *J.*, 1917, 905; *J.*, 1918, 283A.

[65] *Chem.-Zeit.* 1918, 158.

[66] Tetralin, G. m. b. H., Berlin, Ger. Pat. 302003; *J.*, 1918, 348A.

[67] *E.g.* Brölemann, *Muench. mediz. Wochenschr.*, 1918, 65, 674.

[68] *Therap. Monatsh.*, 1918, 32, 368.

[69] G. Maue, *Chem.-Zeit.*, 1917, 41, 689; also *ibid.*, 1918, 176.

[70] A. Foelsing, Ger. Pat. 288338; *J.*, 1916, 385.

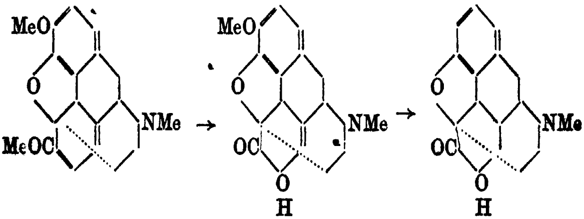
[71] *Biochem. J.*, 1917, 11, 11; *J.*, 1917, 735.

[72] *Z. physiol. Chem.*, 1916, 97, 1.

An efficient disinfection of the intestine is impossible. Experiments have *inter alia* been made with thymol, but the low solubility of this substance in water (1 : 1100) militates against its action. A. Ellinger and L. Adler[74] have obtained some more promising results with *thymol palmitate*, on mice, and also clinically. The ester is much less toxic than thymol, so that larger quantities can be given, and it is hydrolysed in the intestine with the formation of a soap, which keeps the liberated thymol in solution.

HYPNOTICS.

The chief novelty in this section is "eukodal," the hydrochloride of dihydrohydroxycodeinone, introduced by M. Freund and E. Speyer;[75] as a narcotic it has recently been the subject of several favourable reports in German medical literature. The substance is prepared from thebaine (I), which is oxidised by means of hydrogen peroxide



I II III

to hydroxycodeinone (II), in which the position of the hydroxy group is not quite certain. By the use of various reducing agents the hydroxyketone gives three isomeric reduction products;[76] the one obtained with hydrogen and palladium is the dihydro derivative in question (III), formed by the reduction of an aliphatic double bond, and with the keto group intact. The hydrochloride (eukodal) is very stable, and its solutions can be sterilised by heat.

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[73] H. Wieland, U.S. Pat. 1252212; *J.*, 1918, 168A.

[74] *Muench. mediz. Wochenschr.*, 1917, 64, 561.

[75] *Ibid.*, 1917, 64, 380.

[76] M. Freund and E. Speyer, Ger. Pats. 286431; 296916.

Other work deals mainly with the modification of well-known types. Barbituric acid derivatives continue to form the subject of patents, *e.g.* the ethylisopropyl derivative.[77] Compounds of diallylbarbituric acid ("dial") with quinine alkaloids[78] and with alkaloids of the morphine series,[79] particularly one with ethylmorphine, have been protected. These are analogous to similar compounds of veronal.[80] The preparation of "luminal" (phenylethylbarbituric acid) has been described by M. Rising and J. Stieglitz.[81] The methyl esters of phenylacetic and oxalic acids are condensed by means of sodium (after the fashion of the aceto-acetic ester synthesis) and the resulting dimethyl oxalylphenyl acetate, $CH_3O.OC.CO.CH(C_6H_5).CO_2CH_3$ is heated *in vacuo*, when it loses carbon monoxide and furnishes methylphenylmalonate, $C_6H_5.CH(CO_2CH_3)_2$. An ethyl group is then introduced and the resulting ester condensed with urea in the usual way.

Hypnotics which combine groupings from adalin, phenacetine, and urethane in a single molecule, have been protected;[82] they have the general formula, $CEt_2Br.CO.NH.CO.O.Aryl.NH.Acyl$, and are therefore bromodiethylacetylurethanes of N-acylated phenols; the one from *p*-acetylaminophenol may be prepared by condensing bromodiethylacetyl chloride with *p*-acetylaminophenylurethane, $NH_2.CO.O.C_6H_4.NH.CO.CH_3$, in the presence of dimethylaniline, or of bromodiethylacetyl isocyanate with *p*-acetylaminophenol in acetone solution.

The introduction of the *iso*valeryl radicle into the amino-group of aromatic amides preserves the hypnotic property of the latter, but renders them much less toxic.[83] Derivatives with the α-bromo-*iso*valeryl group are especially valuable, *e.g.* cinnamoyl-α-bromo-*iso*valerylamide, $Me_2.CH.CHBr.CO.NH.CO.CH{:}CH.C_6H_5$. According to another patent[84] the *iso*valeryl or bromo-*iso*valeryl-radicle may be attached to the hydroxy group of glycollic, lactic, or mandelic acids; there results, for instance, bromo-*iso*valerylmandelic acid; of this the calcium and quinine salt may be prepared.

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[77] Parke, Davis and Co., Eng. Pat. 105744; *J.*, 1918, 223A.

[78] Ges. für chem. Ind. in Basel, Eng. Pat. 112974, *J.*; 1918, 222A; U.S. Pat. 1261235; *J.*, 1918, 443A.

[79] Ges. für chem. Ind. in Basel, U.S. Pat. 1255423; *J.*, 1918, 193A.

[80] *Ann. Rept.*, 1916, 283.

[81] *J. Amer. Chem. Soc.*, 1918, 40, 723; *J.*, 1918, 322A.

[82] Farbenfabr. vorm. F. Bayer and Co., Eng. Pat. 114680; *J.*, 1918, 282A; Synthetic Patents Co., U.S. Pat. 1256293; *J.*, 1918, 283A.

[83] M. Perelstein und E. Bürgi, Ger. Pat. 297875; *J. Chem. Soc.*, 1918, 114, i. 165.

[84] Chem. Fabrik von F. Heyden, Eng. Pat. 113983; *J.*, 1918, 223A.

LOCAL ANÆSTHETICS.

N-γ-benzoxypropyl-anhydroecgonine ethyl ester ("eccaine") and the corresponding *p*-amino derivative are dealt with in the section on alkaloids. Eccaine is stated to have a stronger anæsthetic action than cocaine, to be non-toxic, and sufficiently stable to allow of the sterilisation of its solutions by heat.

The displacement of the ethyl group in *p*-aminobenzoic ethyl ester by diethylaminoethyl (to form novocaine) is brought about by heating the ester with diethylamino-ethanol and 2% of the aluminium compound of the latter alcohol to 150°–180°. Ethyl alcohol distils off, and the excess of the alkylamino-alcohol is next removed *in vacuo*. After the temperature of the liquid has risen to 170° the residue is poured into cold water and neutralised with hydrochloric acid; unchanged aminobenzoic ethyl ester is removed by filtration. The aluminium compound may be formed in the mixture by adding aluminium amalgam.[85]

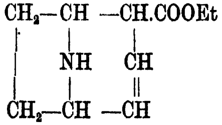
o-Benzoyldiethyl- and *o*-benzoylmonoethylmydriatin, called respectively "allocain S" and "allocain A," are formed by the successive action of an ethyl halide and benzoyl chloride or anhydride on mydriatin (α-phenyl-β-amino-propanol), and are said to be local anæsthetics.[86]

ALKALOIDS.

One of the most important new applications of alkaloids seems to be the use of synthetic homologues of dihydroquinine (alkyldihydrocupreines) as disinfectants; these are, however, dealt with in another section (p. 437). A derivative of thebaine is described among hypnotics.

Another development relates to cocaine and atropine. The ethyl ester of anhydro-ecgonine on demethylation with cyanogen bromide[87] and subsequent hydrolysis is convertible into anhydronorecgonine.

The ethyl ester of the latter substance (annexed formula) may be



alkylated at the nitrogen atom by means of halogen-alkyl benzoates,

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[85] W. Bader and Levinstein, Ltd., Eng. Pat. 111328 *J.*, 1918, 4A.

[86] N. Nagai, Eng. Pat. 117486; *J.*, 1918, 531A.

[87] *Ann. Rept.*, 1916, 287.

e.g. with γ-bromopropyl *p*-nitrobenzoate, which by reduction yields *p*-aminobenzoxypropylanhydronorecgonine ethyl ester, $C_{20}H_{26}O_4N_2$, in which the imino hydrogen atom is replaced by the group—

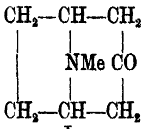
$$CH_2.CH_2.CH_2.O_2C.C_6H_4.NH_2.$$[88]

The new base therefore combines the characteristic grouping of cocaine with that of novocaine. A similar series of reactions has been described by J. von Braun and E. Müller,[89] who state that the demethylation of anhydroecgonine ethyl ester by means of cyanogen bromide gives only a very small yield, and that the same result is achieved more readily by acting on cocaine with cyanogen bromide and then heating with hydrochloric acid. The demethylation of acetyltropine by means of cyanogen bromide has also been patented.[90] The N-γ-benzoxypropyl derivation of anhydroecgonine ethyl ester is designated *eccaine*, and is stated to be more active as an anæsthetic than cocaine, non-toxic, and so stable that its solutions may be readily sterilised. This substance is also referred to in the above quoted patent.

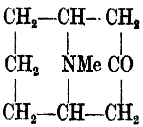
The paper by von Braun and Müller further contains a description of homotropine.[91]

A new type of synthesis of tropic acid has been described by E. Müller,[92] who condenses ethyl phenylacetate with ethyl formate in the presence of sodium, and reduces the resulting hydroxymethylene phenyl, acetate with aluminium amalgam to ethyl tropate.

When tropinone (I) is reduced by means of hydriodic acid or electrolytically it forms tropine from which atropine and homatropine can be prepared, but when reduced with sodium and alcohol it yields ψ-tropine, which does not give mydriatic esters. ψ-Pelleticrine (II), a ring homologue of tropinone, behaves in the opposite way to reducing agents, according to L. F. Werner.[93]



I



II

Here the reduction product with sodium and alcohol (methylgranatoline) yields a powerfully mydriatic tropate and mandelate, whereas the alcohol obtained with hydriodic acid and zinc dust (*iso*-methylgranatoline) yields esters devoid of mydriatic action.

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[88] Chem. Werke Grenzach, Ger. Pat. 301139 (1915).

[89] *Ber.*, 1918, **51**, 235.

[90] Chem. Werke Grenzach, Ger. Pat. 301870.

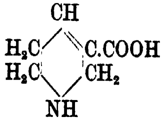
[91] *Ann. Rept.*, 1917, 481.

[92] *Ber.*, 1918, **51**, 252; Chem. Werke Grenzach, Ger. Pat. 302737 · *J.*, 1918, 350A.

[93] *J. Amer. Chem. Soc.*, 1918, **40**, 69.

Ipecacuanha alkaloids.—The addition of two atoms of hydrogen to *o*-methylpsychotrine gives a mixture containing emetine and its stereoisomeride *iso*emetine.[94] The latter base has now been isolated by Pyman,[95] and has been found to be rather less than half as toxic as emetine. Clinically comparatively large doses are tolerated, but appear to have no effect on amœbic dysentery. The above paper contains a useful chart of the interrelationship of ipecacuanha alkaloids and their derivatives. The ethyl, propyl, and benzyl ethers of cephaeline form the subject of a patent.[96] The pharmacology of such ethers and of the natural alkaloids of ipecacuanha has been investigated.[97] Emetine has been used in infection by *Bilharzia*.[98]

Alkaloids of the areca nut.—That the various alkaloids in the nuts of the areca or betel palm are more or less closely related was already indicated by their discoverer, E. Jahns, and several papers which appeared during the current year indicate that they are all, or nearly all, derivatives of a tetrahydropyridine 3-carboxylic acid



originally synthesised by Wohl and Losanitsch.[99] According to Freudenberg[100] the alkaloid *guvacine* is identical with the above; *arecaidine* is its N-methyl derivative, as shown by Wohl and Johnson,[101] and *arecoline*, the principal alkaloid of the nuts, is the methyl ester of arecaidine. Guvacine methyl ester, isomeric with arecaidine, also occurs naturally, and has been termed *guvacoline* by K. Hess.[102] According to Hess and Leibbrandt,[103] on the other hand, guvacine has the carboxylic group in the 4-position and arecaine of Jahns is its

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[94] *Ann. Repts.*, 1916, 228; 1917, 484.

[95] *Chem. Soc. Trans.*, 1918, **113**, 222; *J.*, 1918, 321A.

[96] Farbw. vorm. Meister, Lucius und Brüning, Ger. Pat. 301498.

[97] A. L. Walters and E. W. Koch, *J. Pharm. Expt. Ther.*, 1917, **10**, 73; A. L. Walters, C. R. Eckler, and E. W. Koch, *ibid.*, 1917, **10**, 185; A. L. Walters, W. F. Baker, and E. W. Koch, *ibid.*, 1917, **10**, 341.

[98] M. Mayer, *Muench. mediz. Wochenschr.*, 1918, **65**, 612.

[99] *Ber.*, 1907, **40**, 4701.

[100] *Ibid.*, 1918, **51**, 976; *J.*, 1918, 560A.

[101] *Ber.*, 1907, **40**, 4712.

[102] *Ibid.*, 1918, **51**, 1004; *J.*, 1918, 560A.

[103] *Ber.*, 1918, **51**, 806; *J.*, 1918, 559A.

N-methyl derivative. In his most recent paper Freudenberg[104] has, however, advanced weighty evidence in disproof of the contention of the latter authors, who appear to have wrongly identified the reduction product of guvacine as piperidine-4-carboxylic acid. It follows, according to Freudenberg, that arecaine is not a separate alkaloid but identical with arecaidine, which results when guvacine is methylated with formaldehyde.

Arecoline is poisonous and is used as a vermifuge; the other ester, guvacoline, presumably has similar properties, but the alkaloids with a free carboxyl group have no marked physiological activity. Freudenberg doubts whether these latter alkaloids actually occur as such in the nuts, and considers that they may be formed from the principal ester alkaloids by hydrolysis during extraction. He even questions whether the same does not apply to *arecolidine*, $C_8H_{13}O_2N$ (isomeric with arecoline), isolated in minute quantity by H. Emde,[105] who regards it as 3.4-dimethoxy-1-methyl-1.2-dihydropyridine. Freudenberg thus inclines towards reducing the number of areca alkaloids to two—guvacoline and its N-methyl derivative, arecoline.

GLUCOSIDES.

Apart from a brief note on gitalin,[106] no chemical work on digitalis glucosides has appeared, but attention may here be directed to the considerable number of papers on the physiological standardisation of digitalis which have of late years been published by German pharmacologists, and to the various purified preparations[107] (digalen, digipuratum, &c.) which seem to be used in Germany much more extensively than elsewhere. As was pointed out in a previous report,[108] the chemistry of the glucosides of digitalis is in an unsatisfactory state, and unfortunately this applies more particularly to the "gitalin" fraction, which seems to be therapeutically the most important, since it is soluble in water. The desirability of physiological standardisation was emphasised in a paper by G. B. Roth,[109] who found a variation of 250% in thirteen commercial preparations. In addition to those quoted here, other recent papers dealing with the standardisation of digitalis, &c., have been published by Gottlieb,[110] Holste,[111] and Focke.[112]

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[104] *Ber.*, 1918, 51, 1668.

[105] *Apoth. Zeit.*, 1915, 30, 240; *J.*, 1915, 1270.

[106] J. Burmann, *Bull. Soc. Chim.*, 1917, 21, 290; *J.*, 1918, 136A.

[107] Compare Ullmann's "Enzyklopädie der technischen Chemie," vol. iv., 1916, article Digitalis.

[108] *Ann. Rept.*, 1916, 290.

[109] *U.S. Public Health Service, Hygienic Lab. Bull.*, No. 102; *J.*, 1916, 976.

Although the various glucosides cannot be separated in a weighable condition, it is possible to estimate them separately with a 10% accuracy from October to May by means of physiological experiment on frogs, according to Straub.[113] Cold water extracts from the seeds about 1·3% of active glucosides (*digitalinum verum* and digitalein), and from this solution hardly any active substance is shaken out by chloroform, nor can any more be extracted from the seeds by subsequent treatment with alcohol. In the case of the leaves, about two-thirds of the active matter is extracted by cold water, the remainder (digitoxin) being only removed by alcohol. When shaken with chloroform the aqueous leaf extract gives up "gitalin" but retains digitalein. The minimal lethal doses of all three glucosides have been determined, and by physiological examination of the above alcoholic, chloroform, and aqueous solutions Straub [114] finds that 100 grms. of *Folia titrata* contain 0·24 grm. of digitoxin, 0·375 grm. of gitalin, and 0·37 grm. of digitalein. The following table represents the results of Straub's examination of various commercial and other preparations. The first column gives the number of grams of frog (frog doses F.D.) killed by 1 c.c. of the preparation, *i.e.* the total activity, the second the percentage of gitalin found in the gitalin-digitalein fraction, the third the percentage of digitalein in this fraction (calculated), the fourth indicates the presence or absence of digitoxin, the fifth gives the condition of the gitalin.

	F.D. per c.c.	Gitalin. % found.	Digitalein % calc.	Digitoxin.	Gitalin.
digalen	48·7	54	46	absent	undecomposed
digipan	48·7	54	46	,,	,,
digipuratum	95·2	76	24	present?	partially decomp.
digitalysatum	71·0	75	25	present?	,,
digifolin	48·4	—	—	,,	,,
infusion 4%	46·8	62	38	,,	,,
cold water extract	55·5	46	54	absent	undecomposed

This table shows the considerable difference in the activity of various preparations, already referred to, and further the diminution of activity of an aqueous extract by heating (five minutes at 100°). Digalen, the oldest (1904) and perhaps the best known of the commercial preparations, was described by its originator Cloetta[115] as "digitoxinum solubile," digitoxin in a modified soluble form, but Kiliani[116] had already pointed out that it contained no digitoxin. E. Meyer,[117] in a similar comparative examination of galenical preparations, states that digalen and its copy, digipan, are cold water extracts and owe their activity to gitalin; digipuratum and digitalysatum contain only a portion of the gitalin and correspond to hot water extracts, although the former appears to be made with hot alcohol. The latter is said to be a dealysate of fresh press juice. Meyer also observed that gitalin when dry is insoluble in chloroform, and is not extracted by chloroform from dry leaves; in the presence of a little water it at once becomes soluble in chloroform. In adigan[118] the purification has been effected in a novel manner; digitonin and other undesirable saponins have been precipitated by means of cholesterol, according to Windaus.[119]

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[110] *Arch. exp. Path. Pharm.*, 1918, **83**, 117.

[111] *Z. exp. Path. Therap.*, 1917, **19**, 153.

[112] *Ibid.*, 1914, **16**, 443; *Arch. Pharm.*, 1910, **248**, 365.

[113] *Arch. exp. Path. Pharm.*, 1916, **80**, 52; *J.*, 1917, 734.

[114] *Muench. mediz. Wochenschr.*, 1917, **64**, 513.

By the method already indicated Straub[120] has traced the development of the characteristic glucosides of the leaf; they already appear in the first pair of foliage leaves, which do not contain any of the acid glucosides; in three months the plant is already chemically adult; the active glucosides finally constitute 1% of the dry matter of the leaf (digitalein 0·40%, gitalin 0·35%, digitoxin 0·25%). In another paper[121] he has examined the variations in wild and cultivated plants, and discusses the economics of growing foxglove for medicinal purposes. It would probably pay best to grow only first-year plants, which are chemically quite similar to the flowering ones; the latter alone are admitted to the Pharmacopœia, but the only object of this restriction can be to ensure proper identification. That the first year plants are as active as the flowering ones had already been surmised by R. H. Hatcher,[122] who also insisted that the digitoxin content is no index of activity.

According to Straub,[123] digitalis leaves contain a phenolic glucoside coloured green by ferric chloride (but not a true tannin), which enables a certain amount of active substance, otherwise insoluble, to be extracted by cold water. This or a similar glucoside is present in much larger quantity in oleander leaves, which have a physiological activity

[115] *Muench. mediz. Wochenschr.*, 1904, **51**, 1466.

[116] *Ber.*, 1907, **40**, 2996.

[117] *Arch. exp. Path. Pharm.*, 1917, **81**, 261; *J. Chem. Soc.*, 1918, **114**, i. 367.

[118] *Chem.-Zeit.*, 1918, **42**, 157.

[119] *Ber.*, 1909, **42**, 238.

[120] *Biochem. Zeitsch.*, 1917, **82**, 48; *J.*, 1917, 1193.

[121] *Arch. Pharm.*, 1917, **255**, 198.

[122] *Druggists' Circular*, 1914, 607; *J.*, 1915, 100.

[123] *Arch. exp. Path. Pharm.*, 1918, **82**, 327; *J. Chem. Soc.*, 1918, **114**, i, 252.

about 2½ times as great as that of digitalis leaves; all the active substances are readily subtracted by cold water. According to Straub, Boehringer und Söhne have isolated two crystalline active glucosides; one of these, *oleandrin*, is more active than any digitalis glucoside, and about as active as amorphous *k*-strophanthin; when pure it is almost insoluble in water. Oleander leaves also contain amorphous glucosides in large amount.

Apart from *Strophanthus*, the various other drugs having a digitalis-like action have been little used in therapeutics, or not at all. The claims of squill have been recently advocated by F. Mendel.[124]

Mowrin.—Mowrah seeds (*Bassia longifolia*), which are imported to Liverpool on account of the oil, contain a saponin which remains in the press cake and was first investigated by B. Moore, S. C. M. Sowton, F. W. Baker-Young, and T. A. Webster.[125] It appears to be particularly poisonous to invertebrates, and mowrah meal is a very efficient worm-killer. Mowrin has been recently further investigated by L. Spiegel and A. Meyer,[126] who find it to be a mixture of two substances, the chief of which is the more soluble in alcohol and has the formula $C_{42}H_{68}O_{25}$; on hydrolysis it yields arabinose, lævulose, and mowric acid; the latter is a mixture of crystalline mowragenic acid, $C_{19}H_{28}O_5$, and an amorphous hydrate, $C_{19}H_{30}O_6$.

Uzara.—The root of a species of *Gomphocarpus* (N.O. *Asclepiadaceæ*) is used by medicine men in the region of the great African lakes against diarrhœa. The action of an extract was first described by A. Gürber,[127] and was found to be specific on the intestine, resembling that of opium, but without the undesirable after effects of the latter drug. A dried alcoholic extract, which is obtained from the root in a yield of 25%, was placed on the German market under the name "uzaron." The active principle of uzara has more recently been isolated from uzaron by W. Hennig[128] and named "uzarin." It is a crystalline glucoside, $C_{75}H_{106}O_{30} + 9H_2O$, and is relatively soluble in water, from which it is precipitated by tannin. It is hydrolysed by acids into three molecules of uzaridin, $C_{18}H_{24}O_5$, $\frac{1}{2}H_2O$, three of dextrose, and one of propyl alcohol. Part of the uzaridin is further changed by the acid to anhydro-uzaridin, $C_{18}H_{22}O_4$. The root contains as much as 5% of the glucoside, which is slightly bitter. Uzaridin is strongly bitter.

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[124] *Therapie der Gegenwart*, 1918, 50, 92, 126.

[125] *Biochem. J.*, 1909, 5, 94; *J.*, 1909, 1061.

[126] *Ber. deut. pharm. Ges.*, 1918, 28, 100; *J.*, 1918, 388A.

[127] *Muench. mediz. Wochenschr.*, 1911, 58, 2100; compare also O. Hirz, *ibid.*, 1913, 60, 2220.

[128] *Arch. Pharm.*, 1917, 255, 382; *J.*, 1918, 39A.

ORGANIC COMPOUNDS OF SELENIUM.

During the last half dozen years a certain amount of work has been published relating to organic selenium compounds, for which therapeutic activity is claimed. Although these claims are very far from having been established, the following summary is given on account of the importance of the problem involved—namely, the chemotherapy of cancer. The starting point was an announcement by A. von Wassermann, F. Keysser, and M. Wassermann [129] that they had cured cancer in mice by a selenium derivative of eosin, and this compound was patented by A. von Wassermann and E. Wassermann.[130] Later observers have mostly quite failed to repeat the animal experiments, but some claim a partial success. According to H. Coenen and W. Schulemann,[131] the action of potassium selenocyanide on eosin sodium, under the conditions specified in the patent, merely results in the flocculation of eosin to which some selenocyanide adheres mechanically. To the original patent two additions [132] have been made, which refer to the action of alkali selenides in an inert atmosphere, or in liquid ammonia, on phthalein dyestuffs or their derivatives. The action of selenium halides and oxyhalides on phthalins (obtained by reduction of phthaleins), and the subsequent introduction of halogen, has also been protected.[133] All the products obtained by the above reactions appear to be amorphous, but crystalline derivatives were obtained by treatment of fluoresceins with selenium in alkaline solution, *e.g.* dichlorselenofluorescein.[134] The action of selenium tetrachloride, oxychloride, or tetraiodide on unsaturated acids yields substances such as chloroselenolinolic acid.[135]

It was doubtless the power of methylene blue to stain living protoplasm which led to attempts to prepare its selenium analogue,[136] but according to P. Karrer [137] the processes outlined in these patents do not furnish selenomethylene blue.

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[129] *Deuts. med. Wochenschr.*, 1911, **37**, 2389.

[130] Ger. Pat. 261556 and Fr. Pat. 443554 ; *J.*, 1912, 1025.

[131] *Deuts. med. Wochenschr.*, 1915, **41**, 1213 ; compare also F. Pentimalli, *ibid.*, 1914, **40**, 1468.

[132] A. von Wassermann and E. Wassermann, Ger. Pats. 286950, 287020 ; *J.*, 1916, 107, 171.

[133] Farbw. vorm. Meister, Lucius und Brüning, Ger. Pats. 290545, 291883, 295253 ; *J.*, 1914, 922 ; 1916, 595 ; 1917, 211.

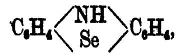
[134] C. Jäger, G.m.b.H., and R. W. Carl, Ger. Pat. 279549 ; *J.*, 1915, 274.

[135] J. D. Riedel A.-G., Ger. Pats. 276976, 287800 ; *J.*, 1914, 1172 ; 1916, 198.

[136] A. von Wassermann and E. Wassermann, Ger. Pat. 261793 ; *J.*, 1913, 783 ; W. Fraenkel, Ger. Pat. 280713 ; *J.*, 1915, 606.

[137] *Ber.*, 1916, **49**, 597 ; *J.*, 1916, 530.

Karrer started from selenodiphenylamine,



$$C_6H_4\left\langle\begin{matrix}NH\\Se\end{matrix}\right\rangle C_6H_4,$$

which is readily obtained from diphenylamine and selenium dichloride in benzene solution,[138] and prepared 3.6-diaminophenazselenonium chloride, and other derivatives. Later[139] he prepared true selenomethylene blue (the tetramethyl derivative of the preceding substance) by treating selenodiphenylamine with bromine in glacial acetic acid until phenazselenonium perbromide is completely precipitated, and then triturating this with an alcoholic solution of dimethylamine. The selenomethylene blue bromide crystallises from boiling water and has the same stability as methylene blue.

The action of selenium or selenium dioxide in concentrated sulphuric acid at a low temperature on aromatic substances such as aniline, phenol, salicylic acid, nitrophenol, &c., has also been protected.[140] Diantipyrylselenide, $(C_{11}H_{11}ON_2)_2Se$, obtained in a similar way, is a crystalline substance; it is perhaps also formed when diantipyryldiselenide (F. von Konek and O. Schleifer[141]) is boiled with hydrochloric acid so as to split off selenium. Alphylselenylureas and their alkyl derivatives[142] are also said to possess marked therapeutic effects, especially towards cancer, but, as was stated above, these claims for selenium compounds are not well founded.

An account of recent work on organic compounds of selenium, from a more theoretical point of view, has been given by F. L. Pyman,[143] where other references will be found.

ANIMAL AND BACTERIAL PRODUCTS.

The ductless or endocrine glands and their hormones are at present being most diligently investigated in America, where a special Association for the Study of Internal Secretions has been founded and publishes a quarterly, *Endocrinology*, entirely devoted to this subject. The chief point of chemical interest is the isolation of the hormone of the *thyroid gland*, already referred to in last year's report.[144] Since then

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[138] W. Cornelius, *J. prakt. Chem.*, 1913, [2], 88, 395.

[139] P. Karrer, *Ber.*, 1918, 51, 190; *J.*, 1918, 263A.

[140] Farbw. vorm. Meister, Lucius, und Brüning, Ger. Pat. 299510.

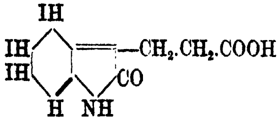
[141] *Ber.*, 1918, 51, 842; *J.*,1918, 560A.

[142] Chem. Fabr. von Heyden, A.-G., Ger. Pats. 305262 and 305263; *J.*, 1918, 389A.

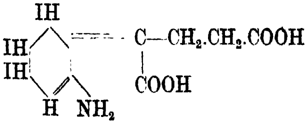
[143] *Annual Reports of the Chemical Society*, 1915, 12, 123.

[144] *Annual Reports*, 1917, 492.

E. C. Kendall has published two further communications. In the former of these [145] he gives the empirical formula $C_{11}H_{10}O_3NI_3$ for the active principle, which he states to be a trihydrotri-iodo-oxyindole-propionic acid, and for which he suggests the name *thyroxin* (being a contraction for thyro-oxy-indole). In a second paper Kendall [146] gives the annexed constitutional formula (I) for thyroxin:



I



II

In the alkaline body fluids he imagines that the substance occurs in the hydrated form (II), and he states in a footnote that a small quantity of thyroxin has been synthesised by his collaborator Osterberg. None of the papers quoted contains experimental details which would permit one to form an opinion as to the soundness of the structural formula put forward, and in particular of the positions assigned to the iodine atoms. The relationship to tryptophane (α-aminoindolepropionic acid), one of the amino acids most indispensable to the animal organism, is very suggestive. There seems to be no doubt about the activity of thyroxin, which is very great. It will do all that dried thyroid gland will do, and it is extraordinarily potent. Many patients have been treated with it at the Mayo clinic since 1912. Thus, for instance, a daily dose containing ⅓ mgrm. of iodine during 11 months increased the weight of a cretin from 16·3 to 22·95 kilos and the height from 92·5 to 116·2 cm. In myxœdematous patients 10 mgrms. increases the basal metabolism by 30%, and hence it is estimated that the total amount of the active principle in the thyroid gland of an adult is 23 to 50 mgrms.

Thyroxin is a crystalline substance melting with decomposition at 220°, very little soluble in alcohol, ether, water, acids, or sodium carbonate, readily soluble in dilute alkalis and ammonia. It reacts *in vitro* with amino acids, its carbonyl group condensing with the amino group and its imino group with the carboxyl of the amino acid. Derivatives in which the carbonyl group is condensed with an amino group, are still active in the animal organism, but if the imino hydrogen is replaced by acetyl, the substance becomes inactive. Kendall imagines that condensation of thyroxin with an amino group of the body is followed by de-aminisation. Presumably the substance is then regenerated, so that its extraordinarily powerful influence on metabolism would be catalytic. The thyroid gland contains no other constituent capable of giving relief in cretinism and myxœdema, but thyroxin represents only half the iodine of the gland; the other half is also in organic combination, but in a non-toxic form, perhaps an intermediate stage in the formation of the active substance.

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[145] *Proc. Amer. Physiol. Soc.*; *Amer. J. Physiol.*, 1918, **45**, 540.

[146] *Endocrinology*, 1918, **2**, 81. See also *J. Amer. Med. Assoc.*, 1918, **71**, 871.

The physiological methods by which Kendall's preparations have been tested are too laborious to be applicable to the examination of commercial specimens of dried thyroid. For this purpose the effect on the metabolism of tadpoles is more conveniently employed. References to this and other methods will be found in the abstract of a lecture by the writer[147] on poisons and drugs of animal origin, which may also be consulted on other points.

Abderhalden[148] has described a method for the purification of organ extracts by subjecting them to body ferments, which do not attack the active principles but decompose the accompanying protein sufficiently to obviate the danger of anaphylaxis from repeated injections. These preparations he calls optones, but whether they will be of any help in the isolation of the active principles seems doubtful. The infundibular portion of the pituitary gland[147] is now extensively employed in midwifery practice, in place of ergot, in the form of extracts (coluitrin, hypophysin, hypophytroin, pituglandol, pituitrin, &c.); the active principle still awaits isolation in spite of various patents.[149] A novel method of testing pituitary preparations has been described by R. A. Spaeth,[150] who used the alteration in size of the melanophores of the scales of certain Atlantic minnows.

E. Berlin[151] has recently found that extracts of the spleen contain, in addition to choline, a substance causing peristalsis of the intestine and contraction of the uterus. This second substance is stated to be precipitated by silver nitrate and baryta and not to be identical with β-iminazolylethylamine. A similar substance is present in the preparation hormonal, introduced by Zuelzer, and alleged to favour intestinal peristalsis. The activity of these substances is probably overrated and non-specific.

Antitoxins.—The principal bacterial antitoxins of proved efficiency are at present those against diphtheria, tetanus, meningococcus, bacillary dysentery, and gas gangrene. "In the early days of the war tetanus of a severe type was common amongst the wounded, and the control of this disease by the prompt administration of a prophylactic dose of antitoxic serum to all wounded men will rank as one of the triumphs of preventive medicine in the war,"[152] in which this serum has been used on an enormous scale. Sera against gas gangrene were not known previously and are a direct outcome of the war; unfortunately they were only produced during the current year. The difficulty here was in the multiplicity of organisms; it is now recognised that one or more of the following anaërobes, "*Vibrion septique*," *B. welchii*, and *B. œdematiens*, play an important part in causing gas gangrene. Sera have been produced against these separately, and these may be mixed together or with tetanus antitoxic serum, or a polyvalent serum may be produced by immunising horses against all three gas gangrene organisms. Like that against tetanus, anti-gas gangrene serum is chiefly used prophylactically but may also be employed therapeutically. In its production the best results have been obtained by the Allies[153]; sera of inferior potency have also been produced in Germany.

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[147] *J.*, 1918, 32T.

[148] *Arch. f. d. gesammt. Physiol.*, 1916, 162, 99.

[149] *Ann. Repts.*, 1916, 294; 1917, 492.

[150] *J. Pharm. Exp. Therap.*, 1918, 11, 209.

[151] *Zeit. f. Biol.*, 1918, 68, 371.

The serum against bacillary dysentery has met with some measure of further success during the war. (Reference to the treatment of amœbic dysentery with emetine was made in last year's report.[154]) In the case of cerebro-spinal fever it became evident, particularly during the epidemic of 1915, that it was necessary to employ only sera prepared from the particular types of organisms of the current epidemic. The right monotypical sera possess considerable curative potency and their employment has been attended with marked success.

A relatively new disease, which has occurred not infrequently during the war, is infective jaundice (Weil's disease), due to *Spirochaeta icterohæmorrhagiæ*, an organism carried by rats. The fact that an efficient anti-serum has been prepared against an organism of this type is interesting, at least theoretically.

Vaccines.— "Enteric fever, the great medical scourge of all former wars, has been reduced in this, the greatest of all wars, to insignificant proportions." This result is mainly due to prophylactic inoculation, which had already proved its worth on a smaller scale in our Indian army. During the present war inoculation was at first limited to vaccines of *B. typhosus*, but since the beginning of 1916 a new triple vaccine, known as T.A.B., and containing in addition *B. paratyphosus* A and B, has been the sole official vaccine for the British army, and has proved efficient in controlling both forms of paratyphoid as well as typhoid fever.[155] In the earlier part of the war the French army suffered somewhat severely from typhoid. The German army has been vaccinated against cholera, as well as against typhoid fever.

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[152] F. W. Andrewes, *Brit. Med. J.*, 1917, i. 831.

[153] C. G. Bull and I. W. Pritchett, *J. Exp. Med.*, 1917, **26**, 867, where an account of further literature is given. See particularly, however, the recent monograph by M. Weinberg and P. Séguin, "La gangrène gaseuse," Paris, 1918, Masson & Cie.

[154] *Ann. Repts.*, 1917, 485.

ESSENTIAL OILS.

The economic conditions affecting the essential oil market in 1917 [156] have continued to operate. Shipping difficulties have increased, and the shortage of spirit has seriously affected the manufacturers of perfumes and of essences. A comparative table of prices [157] for the years 1914–1918 shows in almost all cases a steady upward tendency; the increase is greatest in the prices of synthetics, which, after the initial bound owing to the failure of the German supply, have been affected by high prices of raw materials, shortage of labour, and more recently by the stoppage of imports from America. In July 1914 the price of benzaldehyde was fourteen times, that of heliotropin nine times, that of vanillin nearly five times the pre-war figure. Lemon oil forms a notable exception; the price obtaining before the war has been halved, but the Italian Government has taken control of Sicilian lemon products.[158] An interesting development has taken place in the production of sandalwood oil.[159] About seven-tenths of the world's supply of sandalwood is derived from Mysore, in which state it is a Government monopoly. Formerly 52% was sent to Germany for distillation; the collapse of the market on the outbreak of war induced the Government of Mysore to start the distillation of the oil by modern methods. The first factory, started near the Institute of Science, at Bangalore, was so successful that its output has been more than doubled and a much larger factory is being erected at Mysore which will ultimately be able to produce 20,000 lb. of oil per month, probably sufficient to supply the whole of the European demand. The product of the Government distillery satisfies the requirements of the British and other Pharmacopœias, and each consignment is accompanied by a Government certificate guaranteeing its purity. Since the whole output of genuine sandalwood of Southern India will probably be utilised locally for distillation, European distillers will have to seek other sources of raw material, or cultivate *Santalum album* elsewhere.

The present price of thymol directs attention to possible new sources.

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[155] F. W. Andrewes, *Brit. Med. J.*, 1917, i. 329.

[156] *Perf. and Essent. Oil Rec.*, 1917, 8, 359.

[157] *Ibid.*, 1918, 9, 225.

[158] *Ibid.*, 1917, 8, 317.

[159] *Ibid.*, 18.

Ocimum viride, a perennial native of West Africa, and introduced elsewhere, has been examined at the Imperial Institute[160] and found to yield 0·35–1·2% of an oil containing 32–65% of thymol, no other phenol being present. The plant has been cultivated satisfactorily in the Seychelles. Ajowan seeds grown in the Seychelles are also particularly rich in thymol.

During the year the *Perfumery and Essential Oil Record* has again published various useful summaries on the chemistry of essential oils. The special number dealt with individual terpenes;[161] other articles referred to aliphatic alcohols[162] and to phenols[163] and their derivatives.

Catalytic hydrogenation by means of palladium and platinum has been applied by Paal[164] to terpene alcohols, aldehydes, and acids. Under suitable conditions ethylene linkings may be reduced without affecting alcoholic, aldehydic, or acidic groups, and if several such linkings are present they may be reduced successively. Thus, for instance, citral yields first citronellal and then dihydrocitronellal. The reduction is best carried out with the catalyst deposited on inert powders, as on magnesium, nickel, or cobalt, magnesium oxide, calcium carbonate, barium sulphate, infusorial earth, &c.

The antiseptic value of forty-five essential oils has been investigated by L. Cavel.[165] Under the experimental conditions employed 0·7 part of oil of thyme, the strongest, and 15 parts of patchouli oil, the weakest, were equivalent to 5 to 6 parts of phenol (all per 1000 parts of gelatin broth); the results are in general agreement with older ones of W. H. Martindale.[166] Chlorinated eucalyptol has been suggested as a solvent for the antiseptic dichloramine-T.[167]

Papers of a more theoretical kind on terpenes have been published by O. Wallach and his pupils.[168]

Among recent work on the composition of essential oils we may mention that on oil of sea-samphire[169] from different parts of France, which always contained the three characteristic constituents: 5.6-dimethoxy-3.4-methylenedioxy-1-allylbenzene, the methyl ether of thymol, and crithmene, but in widely differing relative amounts; on gum ammoniac oil,[170] on betulol from oil of birch buds,[171] on the oil of *Artemisia annua*,[172] on that of a *Darwinia* species,[173] and on elemol.[174]

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[160] *Bull. Imp. Inst.*, **15**, 3, 322; **16**, 1, 30. *Perf. and Essent. Oil Rec.*, 1918, **9**, 74, 248.

[161] C. T. Bennett and C. Hollins, *Perf. and Essent. Oil Rec.*, 1918, **9**, 128, 172, 195.

[162] C. T. Bennett, *ibid.*, 105.

[163] L. G. Radcliffe, *ibid.*, 219.

[164] Ger. Pat. 298193; *J. Chem. Soc.*, 1918, **114**, i. 181.

[165] *Comptes rend.*, 1918, **166**, 827; *J.*, 1918, 388A.

[166] Compare *Perf. and Essent. Oil. Rec.*, 1918, **9**, 231.

[167] R. B. Krauss and E. Crede, *J. Amer. Chem. Soc.*, 1917, **39**, 2720; *J.*, 1918, 72A.

[168] See *J.*, 1918, 605A.

[169] M. Delépine and G. de Belsunce, *Bull. Soc. Chim.*, 1918, **23**, 24; *J.*, 1918, 137A.

The pungent principles of ginger were fully discussed last year;[175] since then H. Nomura has patented[176] a synthesis of zingiberone by reduction of vanillylidene-acetone by platinum black. According to a patent of G. Reddelien,[177] carvone anil is an exceptionally delicate reagent for nitric acid, giving a deep blue colour.

Contributions to the physiology of smell have been made by E. L. Backman,[178] who suggests that in order to be odorous a substance must be sufficiently soluble both in water and in lipoids. Thus the lower alcohols are insufficiently soluble in fat, the higher ones in water, but butyl alcohol, sufficiently soluble in both, has a powerful odour. A. Durand[179] suggests that the particles of odorous substances like musk and camphor act as ions in condensing aqueous vapour, and that the sense of smell is dependent on them. This would explain the observed fact that this sense is influenced by the hygrometric condition of the atmosphere. C. van Dam[180] has described a new form of olfactometer.

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[170] F. W. Semmler, K. G. Jonas, and P. Roenisch, *Ber.*, 1917, **50**, 1823; *J.*, 1918, 137A.

[171] F. W. Semmler, K. G. Jonas, and W. Richter, *Ber.*, 1918, **51**, 417; *J.*, 1918, 388A.

[172] Asahina and Yoshitomi, *J. Pharm. Soc. Japan*, 1917, No. 424, i.; *J.*, 1918, 73A.

[173] H. G. Baker and R. T. Smith, *J. Proc. Roy. Soc. N.S.W.*, L 181; *J.*, 1918, 73A.

[174] F. W. Semmler and F. Liao, *Ber.*, 1917, **50**, 1286; *J. Chem. Soc.*, 1918, **114**, i., 25.

[175] *Ann. Rept.*, 1917, 491.

[176] U.S. Pat. 1263796; *J.*, 1918, 389A.

[177] Ger. Pat. 301121; *J. Chem. Soc.*, 1918, **114**, i., 117.

[178] *J. Physiol. Path. gén.*, 1917, **17**, 1; *J. Chem. Soc.*, 1918, **114**, i., 88.

[179] *Comptes rend.*, 1918, **166**, 129; *Perf. and Essent. Oil Rec.*, 1918, **9**, 41.

[180] *Arch. Néerl. Physiol.*, 1917, **1**, 660; *Perf. and Essent. Oil Rec.*, 1917, **8**, 336.

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PHOTOGRAPHIC MATERIALS AND PROCESSES.

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The most serious of the difficulties with which photographic manufacturers in this country have had to contend during the past year has been the shortage of glass, which became so acute as to necessitate not only the still greater use of old negative glass, but the making of an arrangement by which the acceptance of an order is conditional on a supply by the customer of a proportional amount of glass. The value of such glass is much less than that of new glass, partly on account of mechanical defects, such as scratches, but more because of the difficulty of removing all stains, opalescence, &c., produced by the previous treatment. The solution of this problem has not been published, but an idea of the difficulties is given by Waggoner,[1] who found it impossible to make such glass fit for silvering either by the use of strong chemicals or even by heating to softening point. His explanation of a mechanical etching of the surface, less where the silver image reduces the intimacy of contact, will hardly cover all cases in which the surface of glass is affected as regards coating with a sensitive emulsion, and it is more probable that the porosity of the glass, as suggested by Rheinberg, is the cause of the trouble.

The supply of good photographic raw paper, in common with all papers, has been restricted, although several British firms are making excellent base. Baryta coating is being successfully done by several British firms who specialise in this, and also by several photographic paper manufacturers, amongst whom the practice of doing their own baryta-coating is becoming more common.

Suitable packing papers, both for plates and for sensitised paper, have been increasingly difficult to get. Straw-paper especially, which has been extensively used for the packing of print-out-papers, has been almost off the market and there does not appear as yet to be an appreciable quantity made in this country.

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[1] *Phys. Rev.*, 1918, 11, 137; *Sci. Abs.*, 1918, 21, 206.

The supply of good quality photographic gelatin, both British and French, has also been short, the difficulties here being due to poor raw material, combined, in the case of those firms who have only lately taken up the manufacture, with a lack of experience, a matter in which the photographic manufacturer can give only very limited assistance (see later). It would appear, however, that with improved raw material British firms should be able to cope with British requirements both in quality and in quantity.

So far as chemicals are concerned there has been little in the way of actual shortage, although prices have been maintained at a high level. Silver, for instance, has risen from about 3*s.* 9*d.* per oz. at the beginning of the year to about 4*s.* 4*d.* The price of bromides has fluctuated considerably, and the absence of shipping facilities produced for a time a distinct shortage. A small amount of British-made bromide, presumably from American or French bromine, has been on the market, but the bulk of it has come from America. On the whole the quality has been well maintained, although somewhat greater care has been necessary in testing and the proportion of chloride present has shown considerable variation.

The total effect of such conditions to the customer, apart from shortage owing to priority of war contracts, has been a considerable increase of price and uncertainty of supply, but with little if any reduction in quality.

The supply of subsidiary chemicals such as developing agents, sulphite, alkalis, and thiosulphate, has also been maintained, although in some cases at very enhanced prices. All the more important commonly used developers are now made in this country and can be obtained in a satisfactory condition as regards purity. The conditions in America have been as stringent as here, and to judge from the results obtained by H. T. Clarke,[1] adulteration has been fairly common; he gives examples of analyses showing misnaming and considerable adulteration and a list of twenty-five adulterants found in various developers actually on sale.

The production of photographic dyes, more particularly of colour sensitisers, in this country is now well established. The value of this to the Royal Air Force, who used large numbers of panchromatic plates and of colour filters in their observational work, can hardly be overestimated. The range of dyes for purposes such as anti-halation plates, tinting, the making of colour filters and safe-lights, &c., is, however, still very limited, and it is to be hoped that this will soon be put on to a footing comparable with the lists issued by one or two German firms.

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[1] Communication from Eastman Kodak Research Laboratory; *Brit. J. Phot.*, 1918, 65, 499; *J.*, 1918, 784A.

The general question of economy in photographic processes is one which probably needs greater consideration than it has hitherto obtained. The chief sources of waste are glass, paper, silver bromide, and nitrates. The greater part of the waste glass is washed, broken up, and returned to the glass manufacturers. A fair proportion of the waste silver is collected and sent to the refiners for recovery, but there is probably a serious source of waste in very dilute emulsions occurring in certain processes, in which the proportion of silver is so small that it cannot economically be recovered by the usual means. The value of the process of Ilford Limited (Ann. Reports, **2**, 505) for the treatment of such emulsions has now been thoroughly tested and proved. A process has also been introduced in Germany[3] for treatment by metal precipitation, the metal being in the form of balls or rollers maintained in continual motion as the liquid passes through. The ordinary recovery processes also take account only of the silver and not of the bromine generally combined with it; at the present prices of bromine this should certainly be worth recovery. The gross value of the waste nitrates, the bulk of it either the potassium or ammonium salt, is also very appreciable, but its recovery is a more difficult problem because of the great dilution of the solutions; some biological method for utilisation of the nitrogen might be possible, although even that might be interfered with by the small quantity of bromide which is present with the nitrates.

The greatest source of waste, however, and that for which, as far as the writer is aware, no recovery process is in use, is probably the photographic paper—trimmings, &c.; the greater part is contaminated with silver and is burnt in the process of extracting the silver. As photographic paper is made from the best quality rag pulp, a process which recovered that as well as the silver should be very valuable.

One of the most promising events of the year is the formation of the British Photographic Research Association, which has received the support of the great majority of firms engaged on photographic materials or accessories to their manufacture. Captain R. E. Slade, D.Sc., has been appointed director of research, with assistants, and is already at work. The council has adopted a broad outlook on the scope of the work to be undertaken and valuable results should follow.

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[3] Ger. Pat. 302279; *J.*, 1918, 379A.

Negative Processes.

The chief lines on which attention is being directed are X-ray and colour-sensitised materials. In the former very little advance is evident during the past year. Messrs. Illingworth have introduced "Radioprint,"[4] a paper for X-ray negative work; although this cannot be regarded as a general substitute for X-ray plates on account of the much shorter range and lesser detail which an image on a reflecting base must show in comparison with one on a transparent base, it offers distinct advantages for some work by reason of its greater lightness, portability, and freedom from breakage.

In the latter direction Ilford Limited have made a distinct advance with their new Special Rapid Panchromatic plate.[5] In spite of its high speed this plate has a better general colour-sensitiveness than has been previously obtained, and other qualities such as gradation, good keeping, and freedom from veil have not been sacrificed. Some new principle has been adopted for its manufacture, but naturally the details of the process have not been published. The mechanism of the sensitising process is a matter of considerable interest for which as yet no satisfactory explanation is forthcoming. Seyewetz[6] regards it as an accepted fact that in all cases there is the formation of a silver haloid-dye compound similar to a lake; in the case of plates treated with erythrosin, the formation of some such compound appears probable as the dye can be easily washed out from a fixed plate but not from an unfixed plate. To what extent Seyewetz has tested his statement with respect to dyes of the other classes which he mentions —triphenylmethane, acridine, quinoline, &c.—he does not state. It has also been generally assumed that a dye sensitises in the region of its own absorption, but this does not appear to have been carefully tested for at any rate the majority of sensitising dyes; the absorption is not easy to determine since the colour of a dye solution often varies considerably with the solvent, it is not always the same in gelatin film as in water, and the colour of the dyed gelatin film itself is sometimes affected by drying conditions. The absorption would therefore need to be determined as it occurs on the sensitised plate, and this is made still more difficult in some cases—sensitol green and sensitol red for instance—where, as mentioned by Renwick,[7] the light-sensitiveness of the dye is very much greater when in gelatin film containing silver bromide than when in gelatin film alone. There is also the further question as to whether the colour sensitising process adds to the total sensitiveness of the emulsion or transfers a part of the existing sensitiveness to other parts of the spectrum. Considerably more evidence is required on all these points before definite conclusions can be drawn as to the nature of the process, and the complete explanation is probably bound up with that of the latent image, on which subject there is still much diversity of opinion.

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[4] *Brit. J. Phot.*, 1918, 65, 384.

[5] *Ibid.*, 1918, 65, *Colour Supplement*, 28; *Phot. J.*, 1918, 58, 229.

[6] *Brit. J. Phot.*, 1918, 65, 514; *Ibid.*, *Colour Supplement*, 46–47.

[7] Discussion after paper by Pope and Mills on "Photographic Sensitisers," *Royal Phot. Soc.*, Dec. 10, 1918 (not yet published).

For special sensitising to the infra red—as low as $9600\mu\mu$—to allow of the photographic investigation of spectrum lines of metals, the U.S. Bureau of Standards[8] found dicyanin to be the best sensitiser in spite of the chemical fog which it gives, but which for those special researches was not found inconvenient.

Processes for the after-treatment of negatives have been further studied in the Eastman Laboratory. Sheppard[9] has shown the varying activities of different samples of ammonium persulphate as a reducer to be due to the varying iron content, iron acting as a catalyst in the oxidation of silver by persulphate, as Fenton showed it to act in the oxidation of organic acids by hydrogen peroxide.

Nietz and Huse[10] have applied the work of Jones and Wilsey[11] on the spectral selectivity of silver deposits to the question of intensification. Where an intensifying process produces a colour change in the image, the full effect of this change will vary with the colour sensitiveness of the material by which it is to be tested or with the colour of the light by which it is examined. It is therefore only in the cases in which the colour of the image is unchanged that the visual intensification and the effective intensification are the same. A large number of the commoner intensifying processes were examined from this standpoint and their effectiveness determined; the results are unfortunately not capable of quite general application since the effect of an intensifier is partly dependent on the plate with which it is used, a fact which also slightly limited the scope of the investigation.

Colour Processes and Cinematography.

There is no serious advance to report in these sections. A large number of variations in detail are being constantly described and processes patented, chiefly by Americans. It is very difficult to estimate, for any one of these, what its value may be until a process actually in use embodies the detail.

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[8] *U.S. Bureau of Standards*, Bull. 14, 371 [*Sci. Pap.* No. 312]; *Sci. Abs.*, 1918, **21**, 296.

[9] Communication 60 from Eastman Kodak Res. Lab.; *Brit. J. Phot.*, 1918, **65**, 314; *J.*, 1918, 607A.

[10] *Phot. J.*, 1918, **58**, 81; *J.*, 1918, 224A.

[11] *Phot. J.*, 1918, **58**, 70; *J.*, 1918, 223A.

Dufay[12] has brought out an improved method of obtaining a regular colour screen with very fine rulings, in which celluloid film is impressed by a lined roll at a temperature just high enough to soften the celluloid surface. Rulings as fine as 30 to the millimetre are obtained. Colouring is done by filling in the hollows with a greasy ink and staining the upper surface with an alcoholic dye solution. As the method is mechanical both for the depth of the furrows and for the staining, and as treatment of both sides of the celluloid film is possible, thus admitting of a 4-colour scheme, it should be possible to get very satisfactory regular screens by this process. In other processes described there does not appear to be any actually new principle involved; they are chiefly variations in the method of combination of two or three images or of the production of a particular colour. The essential peculiarities of some of the processes are not easily seen, and in one case at least practically the same process was described by one American firm while it was being patented in this country by another American firm.

Theoretical and Experimental.

The standardisation of the measurement of the speed and other qualities of plates and papers, the desirability for which has been strongly urged in some quarters and which at first sight would certainly appear to be a necessity, is by no means a simple problem and it is not yet certain that it is even desirable. A paper by Huse[13] on resolving power illustrates one of the difficulties of standardisation; he shows it to be dependent not only on the plate but on the exposure, the amount of development, and the developer. He used the fan-shaped converging grating and a definite scale of reduction and obtained results to which a numerical value could be assigned. A range of 47 to 77 is obtained by variation of the developer only. Resolving power is also dependent on the colour of the light used, a maximum occurring in the blue, a minimum in the green, and a secondary maximum in the red. This variation is in the opposite direction to that which occurs with "gamma" (steepness of gradation), in which case, according to some recent experiments in the Ilford Laboratories, the results of which have not yet been published, a maximum occurs in the green with minimum in the red and violet. It would seem probable that the variation in resolving power is connected with the opacity of the sensitive film, which, of course, varies with the colour of the light.

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[12] *La Nature*, Nov. 10, 1917, *Sci. Abs.*, 1918, 21, 58.

[13] *J. Franklin Inst.*, 1918, 185, 277 (Communication 61 from Eastman Kodak Res. Lab.); *Sci. Abs.*, 1918, 58, 152.

Jones and Wilsey,[11] in the paper already mentioned on the spectral selectivity of silver deposits, draw attention to the importance and wider bearing of the fact which had been well known for a long time, that the printing value of a negative varies with its colour, a yellow negative giving a more "contrasty" print than one with a similar visual gradation but which is neutral in tone. This, of course, is due to the fact that the sensitiveness of photographic printing materials lies chiefly in the blue and violet region of the spectrum, and the distribution of this sensitiveness not being the same in all papers, it follows that the sensitometric constants of a plate depend not only on the plate itself and its development, but on the printing material with which it is to be used. The importance of this aspect is more evident in problems such as the comparison of different developers, or processes of after-treatment such as intensification (*v.s.*), where the colour of the resulting image may vary considerably.

The sensitometry of X-ray materials is still in a somewhat unsatisfactory position, very little work having been published since the preliminary note by Hodgson mentioned in the last report. One aspect of the subject has been studied by Miss Allen and Laby [14] in Australia, but full details of their work do not yet appear to have reached this country. In the short outline of the scope of their paper given in *Nature* it is suggested that the effect of exposure is dependent on X-ray energy rather than on wave-length. This result is difficult to reconcile with the well-known characteristic radiations, which would have led one to expect very characteristic spectral sensitivity curves from X-ray exposures, and especially with results such as those obtained by de Broglie,[15] who, examining by photographic means the absorption spectra of a number of elements, had first of all to determine the absorption spectra of silver and bromine as shown in the plate itself in order to allow for that effect in the other spectra. With so little of Allen and Laby's paper before us it is, however, impossible to discuss it thoroughly.

The relationship of the absorption of diffusing media with thickness has been studied from a mathematical standpoint by Channon, Renwick, and Storr,[16] and the results, confirmed experimentally, contradict the conclusion of Nutting ("Ann. Reports," 1, 313) that absorption in fully diffused light is proportional to thickness. Renwick has followed up the work by applying the results to a study of the behaviour of diffusing media (pigments) on a reflecting base.[17] The general expression deduced is somewhat complicated; reflection density is given in terms of surface reflection, reflecting power of the base, maximum rejectance of the medium, the thickness or concentration of the medium, and the rate at which the maximum rejectance is reached. A much simpler approximation is obtained in the case of photographic prints, with almost black silver grains with which the maximum rejectance is very small. This expression was checked by experimental observation, and the agreement found was well within the range of experimental error. The expression previously suggested by Jones, Nutting, and Mees ("Ann. Reports," **1**, 312), in which the reflecting power of the silver grains is neglected, is shown to be quite inadequate. The application of the general formula to black image photographic prints is merely the simplest of the possible applications, and its scope may be extended to such cases as sensitive emulsions and coloured pigments, and even to paints, to go outside the photographic boundaries.

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[14] *Nature*, 1918, **102** (Oct. 24), 160.

[15] *J. Roentgen Soc.*, 1918, **14**, 18.

[16] *Proc. Roy. Soc.*, 1918, A **94**, 222; *Phot. J.*, 1918, **58**, 121; *J.*, 1918, 224A.

The density meter designed by Ferguson, Renwick, and Benson,[18] which has several advantages over previously described meters, has aroused considerable interest. It is based on the law of inverse squares, has a horizontal viewing tube, a single light source, a horizontal table large enough to admit of the reading of any part of a half-plate, is calibrated in densities, and will admit of readings up to a density of 2·8 or probably up to 4 with the introduction of a more powerful lamp such as the Pointolite. There is also a reflector for illumination at an angle of 45° on the table of the instrument, a convenient device for the measurement of reflection densities. As the accuracy of the instrument is quite equal to that of other photometers it should find considerable use if it can be produced at a suitable price.

Helmick[19] has obtained some further interesting results on the relationship between exposure and density, testing a suggestion previously made by both Abney and Kron, but without direct experimental evidence. In ordinary plate-speed and characteristic curve determinations, logarithms of exposures are plotted against densities, the exposures being varied either by a time scale or an intensity scale. Helmick has plotted densities against times in a series of exposures in which time and intensity were both varied but in opposite directions, so as to maintain a constant energy, I*t*=constant. He finds in all cases a maximum, *i.e.* for any given value of the product I*t* there is a value of I and a corresponding value of *t*, which gives a maximum effect on the plate. The position of this maximum varies with the speed of the plate—the slower the plate the higher must be the intensity for maximum effect.

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[17] *Phot. J.*, 1918, **58**, 140; *J.*, 1918, 283A. [See also Briggs, "Tinting Strength of Pigments," *J. Phys. Chem.*, 1918, **22**, 216; *J.*, 1918, 273A.]

[18] *Phot. J.*, 1918, **58**, 155; *J.*, 1918, 283A.

[19] *Phys. Rev.*, [illegible], **11**, 372; *Sci. Abs.*, 1918, **21**, 321.

A considerable amount of attention is being directed, in America more particularly, to the properties of gelatin from two aspects. The first is the attempt to get really satisfactory and standardised methods of determining the physical properties of gelatins. The methods[20] are based on and are largely the outcome of those which have been found most suitable for the examination of glues. Apart, however, from the fact that certain minima of strength—setting-power, viscosity, &c.—are necessary and that a stronger gelatin is easier and more economical to work, it is the writer's experience that the physical properties are a very insufficient guide to the suitability of gelatin for making photographic emulsions. There are certain chemical differences between different types of gelatin and even between different batches of the same type, which are more effective than are the physical properties in determining speed, freedom from fog, and such qualities in different types of emulsion. As to the exact nature of these chemical differences there are very few available data, but it is very possible, if not probable, that they are due to the presence or absence of very small quantities of specific substances, rather than to variations in the proportions of the main constituents of the gelatin. A process such as washing the gelatin, for instance, will improve it for some purposes and spoil it for others. The final test of the photographic manufacturer is therefore in the particular emulsion for which the gelatin is required, and the safeguards of the gelatin manufacturer are care in selection of raw material and in its treatment.

The second aspect of the properties of gelatin is being considered largely from a biological standpoint, with the aim of assisting in the elucidation of life-processes. Some of the results have, however, considerable interest to the photographic industry. An instance of this may be cited in the results of Loeb,[21] with which should also be considered the work of Fenn[22] on the precipitability of gelatin by alcohol and the effect on that of acids, alkalis, and salts, that of Fischer, Hooker, and Coffman[23] on the swelling of gelatin in polybasic acids

[20] Sammett, *J. Ind. Eng. Chem.*, 1918, **10**, 595; *J.*, 1918, 631A; Clark and Du Bois, *J. Ind. Eng. Chem.*, 1918, **10**, 707; *J.*, 1918, 665A.

[21] *J. Biol. Chem.*, 1918, **33**, 531; **34**, 77, 395, 489; *J.*, 1918, 274A, 383A, 384A, 520A.

[22] *J. Biol. Chem.*, 1918, **33**, 279, 439; **34**, 415; *J.*, 1918, 216A, 274A, 384A.

[23] *J. Amer. Chem. Soc.*, 1918, **40**, 272, 303; *J.*, 1918, 131A.

and salts, and that of Sheppard and Elliott[24] on the swelling of gelatin in acids and alkalis, and the occurrence of reticulation in gelatin films. Loeb demonstrates the existence of gelatin compounds of the type gelatin-Na (sodium gelatinate) and gelatin-Cl (gelatin chloride) which are produced by the action of salts, acids, and alkalis, the properties of the compounds being strongly affected, however, by excess of reagent. For instance, if powdered gelatin is treated (*a*) with water 6 times, (*b*) with salt (NaCl) solution of $M/4$ or $M/8$ concentration 6 times, and (*c*) with the same salt solution twice and water 4 times, the amount of water absorbed is somewhat lower in *b* than in *a*, but very much higher in *c* than in either of the others; the effect is permanent, the water absorptions being in the same ratio if the gelatins *a* and *c* are melted, dried, and again treated with water. The evidence points to dissociation of the gelatin-metal compound in water, which is inhibited by salts of univalent cations and much more strongly by salts of divalent cations, in proportion to the concentration of the cation. Similar results are obtained in the determination of viscosity and alcohol precipitation numbers (95% alcohol does not precipitate gelatin which has been treated with sodium chloride, and washed with water as in *c* above). In the case of compounds of the type gelatin-Cl, the inhibition of dissociation by salts is determined by the nature of the anion and not by that of the cation. There is, of course, a very close analogy between the treatment of the gelatin in *c* and the washing of an emulsion or of a film to remove excess of salts, one of the commonest of photographic processes.

Note.—As no attempt has been made in this report to refer specifically to every paper which has come to the writer's notice in the period covered, the following references to papers not abstracted in the Journal may be of interest:—Haines, "Cathode-ray Colours," *Brit. J. Phot.*, 1918, 58, Col. Supp., 29; Crabtree, "Dye-toned Images," *Brit. J. Phot.*, 1918, 58, 357; Ives, "Resolution of Mixed Colours," *Phil. Mag.*, 1917, 18; *Brit. J. Phot.*, 1918, 58, Col. Supp. 33; Lux, "Artificial Light in Photography," *Elekt. Zeit.*, 1917, 38, 506; *Sci. Abs.*, 1918, 21, 364.

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[24] Communication from Eastman Kodak Res. Lab.; *Brit. J. Phot.*, 1918, 65, 480; *J.*, 1918, 672A.

LEATHER AND GLUE.

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Research work, both purely scientific and technical, has been very small in quantity during the year 1918, and it is not easy to point to many definite and important advances in either theory or practice. This is of course due to the very small number of men who have been able to carry on research of any kind. The shortage of workmen, high wages, and need for rapid production have had the effect of turning the attention of many manufacturers to labour-economy. This is seen in the adoption of quicker processes, *e.g.* in liming and tanning, and also in the growing desire to lessen the handling of goods by making the fullest possible use of machinery. The effect of the war can also be recognised in the eagerness with which chrome tanning is being taken up by many who, until recently, have never attempted it. Apparently, after a long period of comparative neglect in this country, some effort is now being made to produce those chromed goods hitherto imported on a very large scale. Chrome tanning is not easy or safe without chemical control; indeed many tanners would describe it as impossible. For instance, one cannot regard the different one-bath chrome liquors on the market as equally suitable for all classes of goods, and very awkward surprises are in store for the manufacturer who simply replaces one such liquor by another, perhaps on grounds of cost, without having it analysed and tested. On the other hand vegetable tanning has long been carried on by those whose strictly scientific knowledge was very slight indeed. Probably the reason for the comparatively late adoption and slow progress of chrome tanning in this country lies here, a process such as vegetable tanning, which gives greater scope for simple common sense, being more congenial to Englishmen. Now, however, the usefulness of the chemist in the leather works is widely appreciated, and a striking feature of the war period, and especially of the last year or two, has been the engagement of chemists by firms who had previously relied for success solely on accumulated works' experience. The great factor in this change is no doubt what we have learnt from Germany, but much is due to the fact that vegetable tanning is losing its ancient predominance in the world —not that there is any sign of its disappearance. Tanning is indeed becoming more and more a chemical industry, and chemists are not nowadays kept simply to the control of raw materials and established processes, but, with the more progressive firms at least, are given their due share in the modification of present-day methods and the working out of new ones.

No very great insight is needed to realise the future importance of synthetic tanning materials. Neradol D, brought on to the market just before the war, and apparently doubtfully received, proved to be of such practical importance that several firms in England began its manufacture immediately after German supplies were cut off, and it is probable that at no very distant date the tanner will have as large a variety of synthetic tannins offered him as he ever had of vegetable materials. Further, although Knapp must be pronounced to have been unsuccessful, at least in a commercial sense, in producing iron-tanned leathers, there is no doubt a great field of possibilities in that direction as is indicated by the steady taking out of patents. Knapp could have known but little of the chemistry and physics of colloids, whereas it is now realised how much the success of a process depends on a true appreciation of colloidal conditions. Iron solutions, though similar to chrome solutions in many ways, are far from being exactly like them in a colloidal sense, and in tanning, where ammonia is a strong alkali, and acetic acid a strong acid, conditions must of necessity be very delicately adjusted. Formaldehyde tanning, at present little understood, shows another direction in which the chemist will be of great service to the tanner. Future (and past) work on the reactions of this substance with proteins will have to be very carefully studied by those who wish to develop the process.

Before entering upon a discussion of technical and scientific advances during the year under review, something should be said on the question of raw materials. The leather industry utilises a by-product as its principal material. Hides are always of secondary importance when compared with the carcase from which they are taken, and sheepskins are worth not only less than the mutton, but less than the wool. Consequently, if the best hides and skins are to be obtained, great care with regard to branding, insect pests, flaying, curing, &c., must be taken by those whose chief interest is in food production and not in leather manufacture. Apparently there is in many places a growing interest and activity with regard to the care of hides and skins, of which the world supply is too small to allow of preventible losses. A great effort to eradicate the cattle tick is being made in the United States,[1] which has so far met with pronounced success. The method adopted is to give the cattle an arsenical dip, a treatment repeated every two weeks. Previous to 1909 swabbing and spraying by hand were the methods used, but these were abandoned when dipping was found to be so much more effective. The success attained is shown by the figures for the infected areas. In July 1906 these areas totalled 728,565 sq. miles, and in December 1917 no more than 349,253 sq. miles. The work is still in progress, and vast numbers of cattle have already been saved. In India [2] the Agricultural Department is issuing bulletins and endeavouring by other means to convince cattle owners and others of the great losses they incur by heavy and careless branding, and by unskilful flaying. Branding may easily cause a loss of several shillings per hide, whilst bad flaying may reduce the value to less than half. The opinion is widely held [3] that strong action, even involving international co-operation, should be taken to minimise the preventible loss of hides and hide values, especially at such a time as the present when the number of cattle is very small. It has been estimated that there are 28,000,000 fewer cattle in the world than before the war.

It is now no longer possible to rely on more or less wild trees, &c., for the necessary supplies of vegetable tanning materials. Cultivation has long been practised on the Continent, and it is now being tried extensively within the Empire. A definite endeavour has been made for some years to create a large industry in South Africa by cultivating the wattle and subsequently exporting the bark. A few figures with regard to this may be of interest. Exports in 1908 amounted to 24,849 tons (value £134,562); 1910, 41,344 tons (£219,433); 1913, 65,052 tons (£309,329); 1915, 40,027 tons (£195,244); 1916, 50,866 tons (£254,864); 1917, 41,318 tons (£223,982): 73% of the exports in 1913 came to the United Kingdom, but three-fourths of this was re-exported, principally to Germany. Very great interest is at present being taken in this important industry. Lately the manufacture of a concentrated wattle extract has been taken up in Durban and Pietermaritzburg.[4] One process for the preparation of the extract is on the lines of sugar extraction from the sugar cane and is applicable to the green, undried bark. In another process, also applicable to green bark, the finely chopped material is introduced mechanically into a large leaching vat and moved across it and against a flow of hot water, by means of bronze paddles. The infusion leaves the vat near the point at which the bark enters. Evaporation is carried out in a Multiplex evaporator and vacuum pans, and the finished product is run into gunny bags where it soon sets hard. The wattle extract industry is only in its infancy, the first shipment having been made so recently as 1916, but it is capable of enormous development in view of the excellent qualities of the extract. The wattle industry is also arousing interest in Australia,[5] whilst in India, the cultivation of native tanning materials, *e.g.* "avaram," is also receiving attention.[6] Great difficulties have been experienced during the war, and more especially lately, in securing adequate supplies of tanning materials, and it was found necessary to appoint a Government Committee to deal with the problem and allocate supplies. No doubt the situation will be partly relieved as more and more shipping becomes available, though there must be a considerable shortage for some time to come.

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[1] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 69.

[2] *Leather Trades Review*, 1918, **51**, 730.

[3] *Ibid.*, 1918, **51**, 197.

[4] *Ibid.*, 1918, **51**, 400.

A further effect of the war will be the diversion of the tanning of Indian hides from Germany to this country and to India itself. A regrettable feature of the last few decades was the steady drop in such tanning in this country, and the corresponding steady rise in Germany. For a considerable period before the war, the exports from India amounted roughly to 11,000,000 hides, of which 3,000,000 were tanned, and 8,000,000 raw hides. Immediately before the war, the tanned hides came to England, and the raw hides went to the Continent, whilst at one time, about 1870, all the hides came here.[7] The Leeds district alone used to tan about 3,000,000 kips per annum. All this has been attributed to German commercial methods, but was no doubt largely due to the energetic exploitation of chrome tanning in Germany at a time when English manufacturers were doubtful of its value. Meanwhile large tanneries are being opened in India to deal with the hides in the country of origin, where there are large available supplies of tanning materials, both vegetable and mineral. Action is being taken to improve the general standard of Indian tanning.[8] Another interesting commercial feature is the establishment of large tanneries in Ireland, at Cork and Drogheda,[9] where again hides will be tanned without being first shipped. It is also interesting to notice that difficulties in enemy countries have

[5] *Leather Trades Review*, 1918, **51**, 97.

[6] *Ibid.*, 1918, **51**, 420.

[7] Sir H. Ledgard, *J. Roy. Soc. Arts*, 1918, **66**, 274; *J.*, 1918, 72R.

[8] *Leather Trades Review*, 1918, **51**, 83.

[9] *Ibid.*, 1918, **51**, 146, 580.

been much greater than here. In Germany prizes, amounting in each case to M.20,000, have been offered for (1) substitutes for cod oil and other fish oils used in currying, (2) for substitutes for chrome salts, and (3) for means of economising in the use of vegetable tanning materials.[10]

HIDE STRUCTURE AND PROCESSES PREPARATORY TO TANNING.

The anatomy and physiology of the various hides and skins used in leather manufacture is of great importance, and is very fully dealt with by A. Seymour-Jones in a long series of papers[11] which embody many independent views. For instance, the pelt, *i.e.* the skin from which epidermis and flesh have been removed, is not regarded as simply corium or "true-skin," as is sometimes the case, but as being more complicated in structure, and consisting of "grain-membrane," "fibre-bundle layer," *stratum adiposum*, and corium. The author therefore urges that it is entirely mistaken to regard the pelt used for tanning as being simply composed of fibre bundles, and considers that this view has led to much misunderstanding of wet-work processes. In the "grain" and "flesh" portions obtained on splitting hide or skin we have two things which are structurally entirely distinct. Indeed, instead of regarding the original skin as having two main parts, we must consider it to have three, namely epidermis, true-skin, and corium. These papers (which are excellently and liberally illustrated) cannot, however, be summarised here, though many points of great interest to tanners are discussed. W. Moeller[12] is in agreement with Seymour-Jones in insisting that pelt is not a single protein, and in emphasising the importance of elastin, which is never tanned, but becomes simply encased in tannin, and which does not yield gelatin on boiling. The principal action of bating, according to both authors, is not in the effect on collagen, but in the removal of elastin. Unless this is completely accomplished the necessary softness and "feel" of the finished leather cannot be attained. The presence of elastin is one of the main features of the true skin as distinct from the corium. In other papers Moeller[13] develops a theory of the ultimate structure of the hide and leather fibre, of which the main idea is that hide fibrils consist of chains of ultra-microscopic mixed crystals (micelles) of collagen and its products of hydrolysis. The collagen molecules unite to form crystals, probably polyhedric and elongated in shape, but which tend to a more spherical form on swelling when they become completely surrounded by the decomposition products. In gelatin the collagen micelles have almost all disappeared, and the products of hydrolysis have increased at their expense, forming a network. Tanning causes a twisting of the micelles, a phenomenon which can be observed microscopically. The theory is developed at length, but is not very easily followed, and appears to the writer to outrun the experimental evidence, though of course an ultimately crystalline structure of hide fibre is probable in view of von Weimarn's work on the colloidal state. The difference between the above theory and the views of Procter on the nature of gelatin jelly, *i.e.* that it is a molecular network, is not very great; Moeller holds that there is the formation of ultramicroscopic crystals before the network is formed. It must however be borne in mind that the ultramicroscope gives no proof of structure in gelatin jellies or solutions, and on the other hand that gelatin can be crystallised.

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[10] *Collegium*, 1918, **17**, 197.

[11] *J. Soc. Leather Trades Chem.*, 1917 and 1918, **1** and **2**.

[12] *Coll.*, 1918, **17**, 105, 125; *J. Soc. Leather Trades Chem.*, 1918, **2**, 246; *J.*, 1918, 434A.

[13] *Coll.*, 1918, **17**, 137, 157, 202, 230; *J. Soc. Leather Trades Chem.*, 1919, **3**; *J.*, 1918, 776A.

Liming.—In the practical liming of hides for unhairing there is very considerable advance to report. Acceleration of the process by means of sodium sulphide and other chemicals has been widely practised for many years, but despite the fact that suspension liming was patented by Conyers and Pullein[14] so long ago as 1874, no improvements in the mechanical part of liming have been generally adopted in England until very recently. Now, however, manufacturers are seeking to save time and labour, and rapid methods have come to stay; indeed ten days' liming for sole leather is spoken of as a thing of the past. In the Conyers and Pullein method, hides and skins were simply hung over rails within the pit, whilst spaces were left at the ends of the pit to allow of apparatus for agitation of the lime liquor. Other processes used the same principles. In the old German "Drehkalk" the hides were suspended from arms radiating from a central vertical rotating shaft. The pit was circular and the hides themselves acted as stirrers. Agitation has been secured in other cases by a kind of screw-propeller working underneath the suspended hides (which were protected by lattice-work), by blowing air into the pit (a method still in use), or by rocking the suspended hides. Heating the lime liquor has been suggested by Conyers and Pullein and many others, but seems to be totally unsuitable for sole leather hides, which, although rapidly unhaired, are badly plumped and very loose in the grain. Such processes have, however, failed until recently to meet with general adoption in this country, and the almost invariable method of liming has been simply to allow the goods to lie in the pits. A recently patented process which appears to be very successful is that of T. Melbourne and B. H. Tilson.[15] Hides are slung in the limes by the neck and tail, the hair side being kept uppermost, whilst the liquor is agitated by an oscillating paddle working along the bottom of each pit. The saving in labour is very great, as the hides are never handled from their entering the limes until they are ready for unhairing; the time needed is at least halved, and a great saving in lime is effected. This last point is of considerable interest, for although water will dissolve only a very limited quantity of lime, it is found in practice that large quantities are needed. According to von Schroeder, 6 grms. per litre is sufficient, but this amount, although four or five times as much as the water can dissolve, is much less than is used in practice. Ten pounds of lime per hide is a frequent allowance with ordinary liming methods, whereas with the usual pits, ¼ lb. per hide would produce saturation. However, if an agitation method such as that just described be used, 3½ lb. of lime per hide is sufficient, though this is still a large excess, and shows how much lime is needed to maintain the full strength of the solution in contact with the hide. It is claimed by a writer[16] on the Melbourne-Tilson process that it has many incidental advantages, such as absence of lime stains, decreased loss of hide substance, and the ease with which liquors can be run away. However, any successful mechanical arrangement securing agitation of the liquor and involving suspension of the hides would be sufficiently effective.

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[14] Eng. Pat. 4198, 1874.

Other processes.—There have been no striking developments in deliming and bating during the year under review. H. R. Procter[17] has again called attention to the regeneration of organic acids used in deliming by the addition of regulated quantities of inorganic acids, such as sulphuric acid, to the solution of the calcium salt formed in the process. E. Luksch[18] has patented the use of the waste liquors from the manufacture of tartaric acid for deliming and bating.

TANNING.

The invention of synthetic tanning substances goes on apace, and it is of course impossible to say anything yet with regard to the technical value of the individual products. Some of these substances are of the familiar type obtained by condensing aromatic compounds and their sulphonic acids with formaldehyde.[19] For example, formaldehyde, β-naphthalenesulphonic acid, and naphthalene are allowed to interact in sulphuric acid of non-sulphonating strength. Several recent patents, however, describe the manufacture of tanning substances without the use of formaldehyde, which is quite a step in advance, especially as many of them are made from very cheap materials.[20] For instance, the product obtained by heating Caucasian "naphtha" with sulphuric acid is mixed with phenolsulphonic acid and heated. In another case[21] sulphonic groups are introduced into naphthol pitch or aromatic compounds of high molecular weight. It is evident that the possible sources of synthetic tanning materials are very numerous.

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[15] Eng. Pat. 117581; *J.*, 1918, 555A.

[16] *Leather Trades Review*, 1918, 51, 738.

[17] *J. Soc. Leather Trades Chem.*, 1918, 2, 121 *J.*, 1918, 343A.

[18] Ger. Pat. 305898 *J.*, 1918, 743A.

A. Turnbull and T. B. Carmichael[22] patent a very interesting tanning process involving the use of starch. Vegetable tanning extracts or basic chrome salts are dissolved in starch jelly, with which hides and skins are then treated, either in pits or drums. This process can be used for a great variety of leathers and allows strong solutions to be used safely in the first stages of tanning. The following example may be given to show the strength of liquors used: 500 lb. of chrome alum is dissolved in 125 galls. of hot water, and the solution is made basic by the slow addition of 64 lb. of soda ash previously dissolved in 250 galls. of hot water. The liquor is heated to a temperature above 180° F., and 250 lb. of starch stirred in. The mixture on cooling is used directly for tanning. A quantity of vegetable extract, say 500 lb. at 125° Bark., may be added to the above before the starch. A writer in the Leather Trades Review points out that C. F. Cross similarly employed a strong tannin solution with a vegetable gum as the medium. The writer of this report has seen excellent samples of leather tanned by the starch process.

B. Levin[23] describes a pyrophosphate tannage in which the prepared hides are first treated with an alum solution and then with sodium pyrophosphate. The insoluble aluminium phosphate is thus produced within the hide and not in the tanning liquor, as in the case of an earlier process on similar lines, according to which the sodium pyrophosphate is added to the alum solution and the hides treated with the mixture. Precipitates will enter and in some sense tan hide on drumming. Procter long since showed that tanning could be accomplished with the "insolubles" of quebracho extract; this he regarded, however, as the effect of very slightly soluble substances having great affinity for hide.

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[19] U.S. Pat. 1278229; *J.*, 1918, 743A.

[20] Ger. Pat. 303640; *J.*, 1918, 344A. Eng. Pat. 116933; *J.*, 1918, 520A. Eng. Pat. 116936; *J.*, 1918, 555A. Eng. Pat. 116934; *J.*, 1918, 521A.

[21] Ger. Pats. 304859 and 305777; *J.*, 1918, 477A.

[22] Eng. Pat. 110470 *J.*, 1917, 1244.

[23] Eng. Pat. 117941; *J.*, 1918, 709A

Wood pulp extract is utilised by J. K. Tullis [24] in conjunction with ordinary tanning materials or with sodium bichromate. Patented processes using the ordinary materials are neither numerous nor very novel. L. A. Groth [25] has taken out a patent with regard to his well-known process of electro-tanning, whilst others have patented small modifications of established methods.

An interesting process is described by O. Röhm [26] for improving alum tannages. If the aluminium is used in the form of acetate or formate, or if formic or acetic acid is used with alum, the resulting leather is unusually resistant to water. Röhm [27] has also taken out patents for iron tanning. This he carries out by treating hides with an aldehyde before or at the same time as tanning with iron salts, *e.g.*, hide is treated with formaldehyde in weakly alkaline solution, and then with basic iron chloride. The leather is then neutralised in the same way as chrome leather, or treated with solutions containing precipitants of iron, such as ammonia, phenols, vegetable tannins, &c. This process may be combined with chrome or alum tanning.

There has been considerable interest taken in the sulphur dioxide chrome liquor, *i.e.* the basic liquor obtained by reducing bichromate with sulphur dioxide without the use of any acid. This liquor was referred to by H. R. Procter [28] in the Cobb lectures for 1918, and is now being very widely used, largely on account of the simplicity of its production and the way in which it can be used for many varieties of chrome leather. The writer of this report can testify to its remarkably quick tanning powers. The equation put forward by Procter to represent its formation is:

$$Na_2Cr_2O_7 + 3SO_2 + H_2O = Na_2SO_4 + 2Cr(OH)SO_4.$$

This corresponds to a basicity ratio $Cr : SO_4 = 52 : 96$, a figure confirmed by analysis. Whether, however, the equation represents the true course of the reaction is rather open to question, as Bassett [29] some years ago showed that solutions could be obtained which contained complex ions and did not give the ordinary reactions. The Procter-

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[24] Eng. Pat. 117922; *J.*, 1918, 709A.

[25] Eng. Pat. 116334; *J.*, 1918, 434A.

[26] Eng. Pat. 110750; *J.*, 1918, 217A.

[27] Eng. Pats. 103827 and 104338; *J.*, 1918, 14A, 216A.

[28] *J. Roy. Soc. Arts*, 1918, **66**, 747, 776.

J. Chem. Soc., 1903, **83**, 692.

McCandlish method of analysis involves boiling the solution, and heat is developed in the preparation of the liquor, causing boiling, if pure sulphur dioxide is rapidly led into a strong solution of bichromate. Bassett conducted his experiments with very dilute solutions, which would prevent any considerable rise of temperature. These considerations may be of importance in the preparation of the liquor.

The subject of tanning should not be left without some remarks on the mechanical side of the process. Here again rapidity is aimed at so far as is consistent with a proper quality of leather. Drum tanning for heavy leathers has not been regarded with favour in the past, and it is generally recognised that the process is too drastic. It is, however, possible to tan rapidly with the aid of mechanical means and produce leather as good as the pit-tanned kind. This is done by keeping the hides in motion in the liquors by dragging them through, or by a modified drumming arrangement whereby motion of the hides or liquors is secured, without the sudden bending and stretching, &c., to which leather is subjected in simple tumbling. Such methods are enjoying an increased vogue which has been a notable feature of the last year or two.

ANALYSIS.

Many analytical papers published during 1918 are concerned with the analysis of leather itself, a problem which is certainly not yet completely solved. Early in the year a detailed scheme of analysis was agreed upon by the Government, which, although found to give very uniform results in different hands, cannot be regarded as final.[30] For instance, C. D. Wilkinson[31] soon showed that two hours' drying *in vacuo* cannot give concordant results for moisture unless the pressure is exactly specified. The determination of water-soluble matter gives good agreement, but only, apparently, because the method is given in great detail, and not because all water-soluble matter is removed. The method is, essentially, percolation in a Procter extractor with 1 litre of water at 45° C. for three hours. The determination of nitrogen by Gunning's modification of Kjeldahl's method sometimes involves a very long digestion (though not often with sole leathers, for which the authorised scheme was specially intended) and this is a source of error according to Sörensen's recent work on egg-albumin. Very great importance attaches to the method of preparation of the

[30] *J. Soc. Leather Trades Chem.*, **1918, 2**, 51; *J.*, **1918, 342A.**

[31] *J. Soc. Leather Trades Chem.*, **1918, 2**, 132; *J.*, **1918, 343A.**

sample for analysis, *i.e.* whether it is ground or simply cut up. On this point F. P. Veitch and R. W. Frey[32] have made careful experiments, and not only confirm the usual belief that heating during grinding causes considerable and irregular losses in moisture, but also show that such heating causes similar losses in water-soluble matter. This was certainly not generally recognised before, but the explanation lies in the oxidation and anhydrisation of uncombined tannin, which is thus rendered insoluble. It is possible, as Veitch and Frey showed, to construct a machine of circular saw-blades having specially formed teeth, which will not cause any material heating, but many analysts consider cutting by hand to be much the safest procedure. The Society of Leather Trades Chemists has recently appointed a committee to work on the whole field of leather analysis with a view to improvement and standardisation of methods, and no doubt these points will be taken up.

J. A. Wilson and E. J. Kern[33] have recommended for fat extraction a mixture of equal parts of ethyl ether and carbon tetrachloride. Petroleum spirit, which is usually employed, has not sufficient solvent power, especially in the presence of oxidised fatty acids. Ethyl ether and carbon tetrachloride are each better in this respect, but have disadvantages when used alone. The boiling-point of the tetrachloride is too high for the extraction of leather, and something of the nature of burning is caused. The mixed solvent is free from this objection and is also less inflammable than petroleum spirit. Wilson and Kern also criticise Levi and Orthmann's method of extraction, according to which a definite volume of petroleum spirit is allowed to stand with the leather in a stoppered bottle for 24–72 hours. An aliquot portion of the solvent is then withdrawn and evaporated. In reply, L. A. Levi and A. C. Orthmann[34] state that the mixture of ethyl ether and carbon tetrachloride dissolves much that is neither fat nor oxidised fat from vegetable tanned leathers, and that it removes considerable quantities of dyestuffs and chrome soaps from chrome leathers. They also defend their own method by new experimental results.

T. Mann[35] very fairly criticises the usual mode of stating the amount of sodium sulphate in leather, which is simply a calculation from the sulphates present in the ash, after deducting the equivalent of any magnesium present. Mann argues that a determination of sulphuric acid associated only with soda is impracticable, and gives a convenient method for determining soda itself, since all sodium salts, being soluble, are equally objectionable. The determination of free sulphuric acid in leather has been the subject of a large amount of work by a special committee of the American Leather Chemists' Association.[36] The principal result has been to show the general reliability of the simple Procter-Searle method of evaporating with $\frac{N}{10}$ sodium carbonate solution, igniting, and finally titrating the alkaline ash. Further work is proposed for the investigation of special points. O. Riethof and C. T. Gayley[37] point out the importance of distinguishing the "soluble" from the "insoluble" leather ash, *i.e.* the ash from the water-soluble and insoluble parts respectively of the leather. They show that the sum of these two is always greater than the ash of the original leather unless very great care is taken in this latter determination to wash out soluble salts (*e.g.* sulphates) from the charred leather before igniting.

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[32] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 232; *J.*, 1918, **555**A.

[33] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 138; *J.*, 1918, **343**A.

[34] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 313; *J.*, 1918, **555**A.

[35] *J. Soc. Leather Trades Chem.*, 1918, **2**, 19; *J.*, 1918, **342**A.

Not very much that is new has appeared with regard to the analysis of tanning materials. Here again an American committee[38] has been at work. Sixteen chemists analysed four samples, with disappointing results. The greatest difference between analyses of a powdered chestnut extract was 2·64% of tannin, but in the case of divi-divi, this difference was no less than 12·28%. No doubt there is difficulty in getting uniform samples from a consignment of this material, but for one analyst to find 42·09% of tannin and another 54·37% is disconcerting, especially in view of a long series of results by two chemists published by J. M. Seltzer,[39] in which excellent concordance is shown. It has been usually held that despite the empirical nature of the methods of tannin analysis, very good agreement can be obtained by different workers. There are indeed undeniable theoretical objections to the indiscriminate use of the hide powder process under any or all circumstances. This is well brought out in a valuable paper by J. A. Wilson and E. J. Kern,[40] who deal with the absorption of non-tannins by hide powder. This substance when chromed by shaking with a chromic salt, basic or normal, combines not only with chromium but with acid, sulphuric or hydrochloric. Even after thorough washing with water there is still present ionisable collagen salt. On the basis of the work of Procter and his collaborators on gelatin-acid equilibria, the authors show that the presence of, say, sulphate ions in the hide powder will cause a lessened concentration of electrolytes in the absorbed part of any electrolyte solution, and a corresponding increase in the concentration of the external liquor. For example, after shaking chromed and washed hide powder with potassium sulphate solution, the external solution was found to have a greater concentration by 4·6% (in one case) than originally. Thus, if electrolytes are present in a tannin solution, the external liquid, after shaking with hide-powder, will become more concentrated than before with respect to electrolyte non-tannins, and too high a figure for non-tannins will thus be obtained. Such an error will vary in extent according to the ratio of hide powder to solution. With non-electrolytes, to which Procter's work has not been extended, a similar effect is due to some salting-out effect caused by the ions of the collagen sulphate, provided that the non-electrolyte does not combine with hide powder. Such considerations as the above should have great influence on future improvements in tannin analysis.

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[36] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 319.

[37] *Ibid.*, 1918, **13**, 7; *J.*, 1918, 159A.

[38] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 382.

[39] *Ibid.*, 1918, **13**, 9; *J.*, 1918, 159A.

[40] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 429.

The analysis of chromium compounds &c. has received attention from several writers. J. R. Blockey[41] proposes to determine the basicity of liquors (*i.e.*, the ratio of chromium to SO_4 combined with chromium) by determining the concentration of hydrogen ions in the liquor by means of the hydrogen electrode. This method can, however, be applied only to liquors of the same concentration and made up in the same way, and will be principally useful for dealing with works stock-liquors. A. Harvey[42] points out that if chrome liquors contain ammonium compounds, these must be determined by distillation with alkali. The amount found must be reckoned off the caustic soda used in titrating the boiling liquor for acid combined with chromium, according to the Procter-McCandlish method. C. Smith and F. Enna[43] give a rapid modification of this method. K. Schorlemmer[44] and R. Lauffmann[45] deal with the determination of chromium in presence of iron.

Lactic acid has been the subject of papers by F. C. Thompson and K. Suzuki[46] and by A. Harvey.[47] The latter author gives a useful method for the very necessary determination of iron in commercial acids. The process is based on the colour developed with potassium ferrocyanide, since thiocyanate appears to be useless in lactic acid solution. Thompson and Suzuki, by experiments with pure lactide, show that this substance is an efficient deliming agent. This is not the usual opinion in this country, and tanners have declined to pay for lactide in lactic acid. Further, the separate determination of lactide is not easy, as its concentration is not fixed in a given sample, but varies with the dilution, being highest in concentrated solutions. Time of standing after dilution and temperature also exercise influence. Obviously the amount of lactide present in such a dilute solution as the tanner uses can only by chance be that found by an analyst.

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[41] *J. Soc. Leather Trades Chem.*, 1918, **2**, 205; *J.*, 1919, 82A.

[42] *J. Soc. Leather Trades Chem.*, 1918, **2**, 125; *J.*, 1919, 83A.

[43] *J. Soc. Leather Trades Chem.*, 1918, **2**, 213; *J.*, 1919, 83A.

[44] *Coll.*, 1918, **17**, 145; *J.*, 1918, 445A.

[45] *Coll.*, 1918, **17**, 223; *J.*, 1918, 775A.

[46] *J. Soc. Leather Trades Chem.*, 1918, **2**, 115; *J.*, 1918, 343A.

[47] *J. Soc Leather Trades Chem.*, 1918, **2**, 37; *J.*, 1918, 343A.

One or two papers have appeared on the estimation of sulphides in lime liquors. H. G. Bennett[48] maintains that ammonia is necessary in the solution of zinc sulphate and ammonium chloride used for titrating the sulphide. By this means the precipitation of zinc hydroxide by the lime and the escape of hydrogen sulphide are both prevented. D. McCandlish and J. A. Wilson[49] in reply maintain that this is not the fact. In the case of a lime liquor containing an ordinary amount of sulphide there is no odour of hydrogen sulphide even in the absence of ammonia, whereas with a liquor containing as much as 0·5% of sodium sulphide there is a distinct evolution of gas in the presence of ammonia. H. Hayes[50] suggests modifying the titration by adding excess of the zinc solution to a comparatively large quantity of lime liquor and estimating the excess of zinc remaining. The titrations by the direct method are usually very small, as lime liquors often contain no more than 0·1% of sulphide. In the opinion of the writer there is no need to trouble about great exactitude. An error of 10% in a liquor of 0·1% strength would mean nothing to a tanner.

THEORY OF TANNING, &c.

Vegetable and chrome tanning.—J. A. Wilson[51] replies to Bennett's paper on the theory of tanning,[52] and while admitting the importance of the lyotrope series to which Bennett ascribes such great influence, declares its use in explaining tanning to be unjustifiable, since it is not understood and is unnecessary. Bennett's free use of the term "adsorption" is criticised on account of the vagueness of its meaning, and the view is maintained that many so-called cases of adsorption are instances of chemical combination. The strongest part, however, of Wilson's argument is his development on purely theoretical grounds of equations governing the behaviour of an elastic jelly when immersed in a solution of an electrolyte with which it combines chemically. The equations do not involve any ideas of lyotrope influence or adsorption, but are based on the orthodox conceptions of ionisation and osmotic pressure, and further, they correspond quantitatively with the experimental findings in the case of gelatin and hydrochloric acid. Wilson maintains against Bennett the chemical theory of chrome tanning, on account of the positive charge borne by the particles of a chromic hydroxide sol; as gelatin is also positively charged under similar circumstances, there can be no electrical neutralisation. The writer of this report considers that there is more to be said on this point, as it has never been decisively proved that chromic hydroxide is the tanning agent rather than basic salts. There are strong grounds for believing in the existence of definite basic sulphates, and it has been stated by Stiasny (though the writer cannot find the experimental evidence) that they are negatively charged colloids. The tanning action of a true hydrosol of ferric hydroxide is completely prevented by a protective colloid, such as egg-albumin, whilst the effect of a basic chrome solution is only slightly hindered. At the same time a fact must be mentioned which appears to tell strongly against an electrical neutralisation theory—viz. that chromed gelatin absorbs as much tannin as ordinary material.

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[48] *J. Soc. Leather Trades Chem.*, 1917, **1**, 2; *J.*, 1918, 66A.

[49] *J. Amer. Leather Chem. Assoc.*, 1917, **12**, 633; *J.*, 1918, 66A.

[50] *J. Soc. Leather Trades Chem.*, 1918, **2**, 258; *J.*, 1919, 83A.

[51] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 177; *J.*, 1918, 433A.

[52] *Annual Reports*, 1917, **2**, 370.

Aldehyde and quinone tanning.—W. Moeller[53] vigorously supports a colloidal theory of formaldehyde tanning in opposition to Fahrion. He points out that formaldehyde readily polymerises, especially in presence of alkali (under which condition formaldehyde tanning is carried out) and considers that colloidal polymers are responsible for the tanning effect. Aldehydes which do not polymerise do not tan. Perhaps it is better to say that formaldehyde is the only one with any considerable effect. Further, Moeller questions the reality of the chemical combination of formaldehyde with proteins, though admitting the reaction with products of hydrolysis. W. Fahrion[54] replies that the necessary condition for tanning properties in an aldehyde is the presence of a methylene group united with an oxygen atom, a condition fulfilled by formaldehyde. He also urges that just as this substance reacts with amino-acids, so it can react with the free amino groups which Moeller admits to be present in proteins. Formaldehyde will also tan in alcoholic solution, which disproves the necessity of methyleneglycol, a body which Moeller claims to be the peptiser, formed by the action of water. The whole question is in need of further experimental work, and it should be recognised that a colloidal theory of aldehyde tanning does not stand or fall with Moeller's theory of peptisation. There appear to be, however, strong grounds for regarding the process as simply chemical.

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[53] *Coll.*, 1918, **17**, 25, 61; *J. Soc. Leather Trades Chem.*, 1918, **2**, 188.

Coll., 1918, **17**, 173, 213; *J.*, 1918, 776A.

On the question of quinone tannage, Moeller and Fahrion are again in conflict, the former[55] upholding a colloidal and the latter[56] a chemical theory. Moeller states that the quinones which tan are unstable in aqueous solution and tend to form colloidal solutions. A stable quinone, such as anthraquinone which does not form colloidal complexes, does not tan. Moeller regards quinone tannage as an oxidation of free amino-acids present in hide, with the formation of quinol and quinhydrone; the oxidation proceeds to the formation of colloidal humins which are the essential tanning agents. Fahrion regards the process as simply a chemical combination which will take place on rubbing together dry quinone and hide-powder. If the product is extracted with alcohol and dried, it is found to be very resistant to water, and is therefore leather. The instability of quinone in aqueous solution is consequently irrelevant, and Moeller's peptisation theory is dismissed as superfluous.

Swelling &c. of gelatin.—H. G. Bennett[57] develops a new theory of the swelling of gelatin on very different lines from that of Procter. The contractile force of surface tension causes any liquid surface to be a zone of compression, and any increase in surface causes a corresponding extension of such zones. In a gelatin sol an enormous surface is developed by the particles of the disperse phase, and consequently the compressed water is a considerable proportion of the total amount present. With increasing concentration there is gradual approach and ultimate contact of compression zones with a corresponding increase in viscosity, finally resulting in rigidity. Rise in temperature increases the kinetic energy of the particles and reduces the compression with consequent loss of viscosity. The structure of a jelly is therefore a continuous network of water under great compression. A jelly, even when immersed in water, has a surface tension which tends to resist swelling, and depends on the extent of the compression in the water of the jelly. As the jelly swells, therefore, the power of resisting swelling diminishes. Dissolved substances have an effect on the compressibility and other physical properties of water called the lyotrope effect, and strongly influence the compression of water in a jelly. Substances with a small or great lyotrope effect have a corresponding effect on the properties of gelatin jelly. Some dissolved substances in concentrated solution produce a stronger effect of compression than exists in the original jelly; the surface tension effect is therefore reversed and the jelly contracts and hardens. The repulsion of similarly charged particles is held to be the cause of swelling. This force diminishes rapidly with increasing volume until it is less than the more slowly diminishing contractile force. On the above grounds, assuming the electrical charges to be due to adsorbed ions, Bennett gives an equation for the force producing swelling, and deduces from it curves which correspond in type to those experimentally obtained. H. R. Procter,[58] in reply, objects to the term "lyotrope influence," as not conveying any definite meaning, and emphasises the purely qualitative nature of Bennett's reasoning, whilst pointing out that his theory of acid swelling, as due to the osmotic pressure of ions associated with the colloid, accounts quantitatively for the observed facts. Procter's most serious objection to Bennett's theory concerns the statement that the surface of a liquid is in compression on account of surface tension. This he regards as mechanically impossible, as pressure momentarily set up in the surface layer would be immediately transmitted to the interior mass of liquid. The surface is actually a region of tension and lessened density. In any case compression does not cause large increases in viscosity. Further, colloid particles, though charged, are surrounded by an oppositely charged layer of ions, giving an electrically neutral complex. Thus no electrostatic repulsion can take place. Charged particles move in electrophoresis because the layer is continuously displaced in an opposite direction to that of the particle. A simple account of Procter's theory of swelling is given in the Cobb Lectures on "Recent Developments in Leather Chemistry."[59]

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[55] *Coll.*, 1918, **17**, 71, 93, 210, 241; *J.*, 1918, 776A.

[56] *Loc. cit.*

[57] *J. Soc. Leather Trades Chem.*, 1918, **2**, 40; *J.*, 1918, 314A.

V. Kubelka[60] has recently published work on the absorption of acid by hide powder. In the case of pure hydrochloric acid the amount taken up is independent of the concentration of the acid solution. For instance, from acid varying in strength from $\frac{N}{100}$ to $\frac{N}{1}$, 1 grm. of dry hide powder fixes 0·739 millimols of hydrogen chloride. In the presence of sodium chloride the phenomena are more complex, and the absorption curve consists of two branches, the first reaching a maximum corresponding with the absorption of 1 grm.-mol. of hydrogen chloride by 977 grms. of hide powder. The author regards this as indicating the formation of a definite compound, and considers 977 to be the molecular weight of collagen. The second branch of the curve is of the normal adsorption type, showing that the compound first formed simply adsorbs further quantities of acid. The conclusion that a definite compound is formed is the natural complement of Procter's discovery in the case of gelatin and acid

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[58] *J. Soc. Leather Trades Chem.*, 1918, **2**, 73; *J.*, 1918, 314A.

[59] *J. Roy. Soc. Arts*, 1918, **66**, 747, 776.

[60] *Kolloid. Zeits.*, 1918, **23**, 57; *J.*, 1918, 665A.

A large amount of work on gelatin, fibrin, &c., from the biological standpoint has been published in America. M. H. Fischer[61] and others have worked on the swelling of gelatin and fibrin in solutions of polybasic acids and their salts, and find that with gelatin in phosphate solutions minimum swelling occurs in a solution having the composition of practically pure monosodium phosphate. In citrate solutions the minimum swelling takes place in a solution of 40% of monosodium and 60% of disodium citrate. Fibrin has minimum swelling in rather different solutions. The work is vitiated by neglect to analyse the external solutions after the attainment of equilibrium. There are alterations in the composition of any solution in which a protein swells, and these have been ignored by the authors. A similar error is made by R. C. Tolman and A. E. Stearn,[62] who have studied the swelling of fibrin in acids. They assume that the acid absorbed is of the same concentration as the external liquid, which is quite contrary to the facts. It is interesting to note that these authors, like Bennett, attribute swelling to electrostatic repulsion of charged particles. W. O. Fenn[63] has worked on the effects of electrolytes on gelatin. He finds, for instance, that the amount of alcohol required to precipitate gelatin increases with increasing concentrations of salts in solution. Very small amounts of alkalis and acids entirely prevent the alcohol precipitation, whilst with larger amounts, the quantity of alcohol required diminishes slowly with increasing concentration of electrolyte. This hindering action of akalis and acids in small quantities is diminished by univalent salts such as sodium chloride. Divalent cations such as calcium are antagonistic to alkalis, but not to acids; the reverse is the case with divalent anions. J. Loeb[64] has also published several papers on gelatin. He finds that this substance after soaking in sodium chloride solution will swell much more in water or a weaker salt solution. This has, however, long been known through Procter's work, and Procter's view of swelling as due to the formation of ionisable gelatin compounds is put forward as the explanation. Loeb also finds that a divalent cation such as calcium causes contraction, and this he regards as due to the formation of a non-ionisable compound. The limiting concentrations of neutral salts which just inhibit the additional swelling of gelatin depend on the valency and not on the nature of the ions. Experiments on the influence of electrolytes on other properties of gelatin, such as osmotic pressure, viscosity, and precipitation by alcohol, show a distinct parallelism with the results on swelling.

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[61] *J. Amer. Chem. Soc.*, 1918, **40**, 272, 292, 303; *J.*, 1918, 131A.

[62] *J. Amer. Chem. Soc.*, 1918, **40**, 264; *J.*, 1918, 131A.

[63] *J. Biol. Chem.*, 1918, **33**, 279, 439; **34**, 415; *J.*, 1918, 216A, 274A, 384A.

[64] *J. Biol. Chem.*, 1918, **33**, 531; **34**, 77, 395, 489; **35**, 497; *J.*, 1918, 274A, 384A, 520A, 709A.

Chrome liquors.—Some interesting papers on the nature of basic chrome liquors have appeared. A. W. Thomas and M. E. Baldwin[65] have studied the acidity of these liquors by means of the hydrogen electrode and have obtained instructive results. The writer however sees no force in the authors' strictures on the basicity figure. This represents the ratio of chromium to sulphuric acid combined with chromium, and is variously expressed, in this country usually as 52 : x. For instance, $Cr_2(SO_4)_3$ has the ratio 52 : 144, and $Cr(OH)SO_4$ the ratio 52 : 96. Such a figure, obtained by analysis, gives the empirical composition of the chromium compounds in the liquor, and is valuable information from the tanner's point of view, as variations in basicity mean very real differences in the tanning effect. The acidity of a liquor is due to hydrolysis, *e.g.*—

$$Cr_2(SO_4)_3 + 2H_2O \rightleftarrows 2Cr(OH)SO_4 + H_2SO_4.$$

The extent of this hydrolysis varies with dilution and temperature, but it in no way corresponds with the basicity of the chrome compound. Thomas and Baldwin, however, criticise the basicity figure because it bears no relation to the acidity as found by the hydrogen electrode, whereas, in this country at least, no one supposes that basicity figures reveal anything else than the empirical composition of the liquor. The authors found that moderate dilution of a basic liquor caused an immediate drop in hydrion concentration and a further slow decrease in the course of several days. Very great dilution, however, caused an immediate drop to a final value. The decrease in hydrion concentration in this case does not correspond exactly with the dilution, but represents a greater degree of hydrolysis. A stock liquor, for instance, with $[H^\cdot] = 0{\cdot}0049$, was diluted to twenty times its volume, when $[H^\cdot]$ fell immediately to 0·0008, and after seven days further diminished to 0·00055, thus showing a final degree of hydrolysis rather more than twice the original. However the interpretation of this last result is complicated by the settling out of a precipitate. A concentrated chromic sulphate solution behaved rather differently, the immediate drop in hydrion concentration corresponding roughly to the dilution, after which ensued a slow increase to a final equilibrium value. A very valuable feature of the paper is the experimental proof afforded that the hydrolysis of chromium compounds at ordinary temperatures is a very slow process. J. R. Blockey[66] also publishes work on chrome liquors and verifies the greater hydrolysis of green as compared with violet chromium solutions. The hydrion concentration in the former is over ten times that in the latter. It is a well-known fact that green solutions swell pelt much more than violet ones, and generally behave (in the inversion of cane sugar for instance) as being more acid. Green solutions are produced by boiling, and according to Blockey the colour is probably due to chromium ions. whilst the unionised compound is violet.

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[65] *J. Amer. Leather Chem. Assoc.*, **1918, 13, 193; *J.*, 1918, 434A.**

[66] *J. Soc. Leather Trades Chem.*, **1918, 2, 205; *J.*, 1919, 82A.**

Another paper by Thomas and Baldwin [67] deals with the rôle of neutral salts in chrome liquors. The effect, as yet unexplained, of sodium and ammonium chlorides is to increase the hydrion concentration very considerably. This is even the case when salt is added to dilute sulphuric acid. Sodium and ammonium sulphates retard the formation of a precipitate on dilution, and the effect increases with the amount used, but there does not appear to be any definite hydrion concentration at which precipitation begins.

Chemistry of vegetable tannins.—Nothing has recently appeared of such great interest as E. Fischer's investigation of gallotannic acid referred to in the report for 1916. The same chemist has, however, continued work on tannins and tannin derivatives, and has recently carried out a new synthesis of digallic acid.[68] 3.5-Diacetylgallic acid is condensed with triacetylgalloyl chloride, yielding penta-acetyl-*p*-digallic acid. Curiously enough, when this compound is hydrolysed with cold dilute ammonia *m*-digallic acid is formed. Another paper by Fischer [69] on chebulic acid shows that although this substance yields gallic acid and dextrose on hydrolysis, it is not related in structure to the galloyl-glucoses.

GLUE.

There is little to report under this head. A. W. Clark and L. DuBois [70] have published a paper on the "jelly value" of glues and gelatins, in which they give details for determining the weakest solution which gives a solid jelly at 10° C. If a 6% solution of a sample is solid at this temperature whilst a 5% solution is liquid, the material is said to have a comparative jelly strength of 6%. C. F. Sammet [71] measures jelly strength by determining the ease with which swollen particles of glue melt and slide when placed on an inclined brass plate, one end of which is dipped in water at 40° C. The poorer grades melt and slide down the plate more rapidly than the better glues. A method for directly determining the adhesiveness of glue has been worked out by M. Rudeloff.[72] The sample should be dissolved in 150% of water, and the solution applied to wooden surfaces carefully prepared and of prescribed area. The wood should have been previously heated in dry air at 40° C., and after the glued surfaces are brought into contact, the film is left to dry under a pressure of not less than 0·84 kilo. per sq. cm. The force required to pull apart the two pieces of wood is then measured by a suitable machine.

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[67] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 248; *J.*, 1918, 555A.

[68] *Ber.*, 1918, **51**, 45.

[69] *Ber.*, 1918, **51**, 298; *J.*, 1918, 274A.

[70] *J. Ind. Eng. Chem.*, 1918, **10**, 707; *J.*, 1918, 665A.

[71] *J. Ind. Eng. Chem.*, 1918, **10**, 595; *J.*, 1918, 631A.

[72] *Mitt. K. Materialprüf.*, 1918, **36**, 2; *J.*, 1918, 743A.

AGRICULTURAL CHEMISTRY.

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In order that the recent work of agricultural chemists may be properly understood it is necessary briefly to refer to the changes in position brought about by the war, especially in its later phases.

At the outbreak of war the country raised about one-half of its total food, excluding beverages such as tea, coffee, and wine, which could not be produced here even if they were counted as foods. Some commodities were produced in less quantity than others: we produced nearly all our milk, but only a small part of our bread. For many years the cultivation of wheat had declined, until only about ten weeks' supply was grown here each year, the rest being imported from North and South America, Australia, Russia, Roumania, &c.[1]

For the first two years of the war there was general acquiescence in these conditions: food came into the country, and optimistic views were held as to the duration of the war. The home production fell, and was at a low ebb in 1916. At the end of 1916, however, the new Government adopted a new policy. The war was making increased demands on shipping, and the submarine menace emerged into reality: food could no longer be imported on the same scale as before. A programme for increased home production was therefore worked out and a body of experts set up to deal with the technical problems involved. A wholly new conception was introduced: hitherto the farmer, like any other business man, had worked frankly for profit; he had been left to decide his own plans and had adopted whatever course he thought best; the merits of his methods had been judged solely by the amount of profit they had yielded. Now, however, the farmer was required to grow food: calories, and not pounds, shillings, and pence, were to be the guiding consideration. County Councils were given drastic powers of compulsion, which, however, it is pleasant to record, have only rarely had to be used, the patriotism of the farmers being a sufficient incentive to the great endeavour they had to put forth.

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[1] For an able discussion of the food situation, see T. B. Wood, *The National Food Supply in Peace and War*, Camb. Univ. Press, 1917.

In passing from money units to food units, it became necessary to alter considerably the scheme of husbandry. Meat production on grass-land, one of the most lucrative branches of farming, was shown to yield only a fraction of the food per acre given by corn and potatoes.[1] Consequently, the order went forth that a certain proportion of grass-land must be ploughed up and planted with corn or potatoes. This programme gave rise to many of the technical problems that have occupied the attention of the agricultural chemist.

A second series of problems arose out of the need for fertilisers. In peace time this country had exported fertilisers not because they were unnecessary for our soils, but because the type of farming commonly adopted did not call for much fertiliser. The new food production programme, however, required considerably more; but, unfortunately, a competitor appeared who would not be denied. The common fertilisers were: superphosphate (made from African rock phosphate and sulphuric acid), sulphate of ammonia (made from ammonia and sulphuric acid), nitrate of soda (imported from Chili), and potassium salts (imported from Germany). Of these, the Ministry of Munitions claimed the whole of the nitrate of soda, much of the ammonia, and a large proportion of the sulphuric acid; while the import of potassium salts from Germany naturally came to an end. Thus at the very time when the need for fertilisers was greatest the supply threatened to be cut off. Had labour been available the difficulty might have been mitigated; but, unfortunately, there came at the same time an imperative call for men.

It will always be a credit to the British farmer and a source of pride to the administrators and expert advisers that in these difficult circumstances the food production of the country was not only maintained, but markedly increased: 1916 had been one of the lowest years on record; 1917 showed a marked improvement; and 1918 a still greater improvement, the production of food being greater than in any previous year on record.

FERTILISERS.

In relating the story of these achievements, it will be convenient to begin with an account of the work on fertilisers. By far the most important fertiliser on the farm is farm-yard manure, of which some 37 million tons were, prior to the war, consumed annually, against only 1·2 million tons of all artificial fertilisers added together. Unfortunately, the method of handling the manure leaves much to be desired: it is estimated that about 50% of the nitrogen is lost during the making and storage. Investigations were therefore begun of the causes of this loss of nitrogen with the view to the discovery of methods of control. It was shown[3] that the loss is caused partly by leaching and partly by biochemical decomposition, resulting in an evolution of gaseous nitrogen. No loss occurs, however, under anaërobic conditions, nor could any be detected under rigidly aërobic conditions; a mixed condition of aeration seemed essential, indicating that the evolution of nitrogen is not a simple oxidation or a simple reduction, but a complex change involving both types of action. The practical deduction is that farm-yard manure must be kept as sheltered as possible and stored under conditions as nearly anaërobic as they can be made.

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[1] T. H. Middleton, *J. Bd. Agric.*, Sept. 1915; E. J. Russell, *J. Farmers' Club*, Nov. 1917.

Simultaneous investigation was made of the liquid manure draining away from cow-stables. Farmers had always known its value as manure, though they had not usually acted up to their knowledge, and demonstrations had been made of its value in comparison with other fertilisers.[4] Arrangements were put in hand to improve the manure-tanks, but unfortunately they have not yet materialised.

Numerous attempts have been made to replace the sulphuric acid required in making ammonium sulphate by nitre-cake, of which quantities were available. Nitre-cake readily absorbs ammonia, and its use involved no insuperable mechanical troubles, although there were undeniable troubles in connection with the mother liquor: the chief difficulty was to secure a uniform product.

The replacement of sufficient acid to reduce the ammonia content from 24 to 18/20% was tolerably easy, and agricultural trials showed that the new material on equal nitrogen basis was of the same value as the old standard material.[5] But serious troubles were experienced when a large replacement was attempted. An investigation was therefore made of the equilibrium in the system—ammonium sulphate, sodium sulphate, and water.[6] This showed that the double salt $(NH_4)_2SO_4.Na_2SO_4,4H_2O$ is not formed above 58° C.; and if, therefore, in a continuous process the resultant solids are fished at a temperature above this, they will consist of the two separate sulphates. Later published work showed that sulphate of ammonia tended to separate out when the liquid was concentrated at or near the boiling-point, so long as the ratio of ammonium sulphate to sodium sulphate in the residual hot liquor does not fall below 2·7. On the other hand, sodium sulphate crystallises out when the liquor is cooled. One possible method of separation, therefore, would be alternate heating and cooling.[7] The "Badenor" process was more promising, however; its essential feature was that a solution already saturated with sodium sulphate was used to wash out acid from the nitre-cake.[8] Since the signing of the armistice, however, acid has been liberated and the problem has disappeared.

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[3] E. J. Russell and E. H. Richards, *J. Agric. Sci.*, 1917, 8, 495–563, for the scientific work; *J. Roy. Agric. Soc.*, 1917, 77, 1–35, for practical details. See *J.*, 1918, 35A.

[4] *E.g.* J. Hendrick, *Aberdeen Coll. of Agric.*, *Bull.* 19, 1915.

[5] *Annual Report, Rothamsted Expt. Sta.*, 1914–17, p. 66.

[6] Private communication, Messrs. Brunner, Mond and Co., Ltd., 1917.

A wholly different method has been suggested in Japan.[9] Ammonia gas and carbon dioxide are passed into a solution of sodium sulphate, when sodium bicarbonate is said to be precipitated and ammonium sulphate left in solution. Improvements in the manufacture of ammonium sulphate by the Adam process have led to a reduction in acidity.[10]

Other sources of nitrogenous fertiliser have been vigorously explored. At the present time sewage is under examination. For many years serious efforts have been made to produce a useful manure from this source. Many calculations have been made to show the value of the material lost in sewage; but nothing acceptable to agricultural chemists could be prepared—the value of the ordinary sludge being often more sentimental than real. Recently, however, a new method of procedure has been evolved, yielding the so-called activated sludge, which, apparently, possesses considerable fertilising value. It contains when dry no less than 6% or 7% of nitrogen instead of the old 1% or 2%, and, further, in the preliminary experiments, the effectiveness of the nitrogen has proved to be of a much higher order than that of ordinary sludge. More precise experiments would be needed to determine what proportion of sewage nitrogen is recoverable; but, so far as we can judge, the problem is so important that an extended trial is called for.[11]

Another possible source of nitrogen fertiliser is peat, which has always proved alluring to inventors. One of the best-known attempts at utilisation was that of W. B. Bottomley. It consisted in a bacterial treatment, whereby the peat suffered a double change with formation of the so-called auximones and fixation of gaseous nitrogen. When used for potting-purposes, the material is said to have given satisfactory results; but it was unsuccessful in the field-trials carried out at Rothamsted and the Harper Adams Agricultural College.[12] The subject bristles with difficulties, but is so important that further efforts might well be made in spite of the first failures. Various patents have been taken out for the production of ammonia from peat by distillation, but nothing has yet been done on the large scale—the preliminary drying having proved a serious difficulty. During the war period, at any rate, peat made no appreciable contribution to our fertiliser resources. The peat resources of Canada have attracted attention.[13]

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[7] H. M. Dawson, *Chem. Soc. Trans.*, 1918, **113**, 675–688, for theoretical data and considerations see *J.*, 1918, 577A.

[8] P. Parrish, *Gas J.*, 1918, **143**, 365–366; details are also given of manufacture as adopted at Stafford and Llwynpia (Glam.); *J.*, 1918, 577A.

[9] T. Fujiyama, Eng. Pat. 116321, *J.*, 1918, 466A.

[10] *J.*, 1918, 441R.

[11] There is now an extensive literature on this subject: see the important papers by Ardern and his co-workers, summarised in the *Journal*, 1917, 822.

A further possible source of fertiliser is seaweed, valuable not only for its nitrogen, but also for its large content of potash. Serious efforts have been made by Hendrick in Scotland to induce some competent body to undertake the exploitation on a proper scale, but, so far, without success.[14] In Ireland the kelp-burners have been kept as busy as possible [15] in attempting to supply the needs of the flax-growers of North Ireland, to whom potash is an indispensable fertiliser. Numerous proposals have been made to set up factories where the various by-products could be recovered; and, indeed, it is reported that a company is about to start operations in Sweden.[16] A good deal of seaweed is used as manure by farmers near the coast; but much is wasted, and there certainly seem possibilities of better utilisation. As in the cases of peat and sewage, the great practical difficulty is the preliminary drying.

Prior to the war a new branch of the fertiliser industry had been founded, the production of calcium nitrate and cyanamide synthetically from the gaseous nitrogen of the air. During the war these substances have been taken for munitions, but with the coming of peace they will again be available to the farmer. Numerous trials have shown that calcium nitrate is usually as effective as sodium nitrate,[17] and it has the further advantage that it does not induce a sticky condition in heavy soils, such as sodum nitrate sometimes gives through the sodium carbonate formed on its decomposition. The makers have taken out a patent for neutralising the nitric acid with a mixture of rock phosphate and limestone, which is said to yield a hard, dry mass of considerable fertilising value.[18]

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[12] E. J. Russell, *J. Bd. Agric.*, 1917, **24**, 11; *J.*, 1917, 514.

[13] B. F. Haanel, *J.*, 1918, 258T.

[14] J. Hendrick, *J.*, 1916, 565; see also C. Sauvageau, *Revue gén. des Sciences*, 1918, **29**, No. 19.

[15] *J.*, 1918, 323R.

[16] *J.*, 1918, 279R.

[17] For example, J. Hendrick, *J.*, 1918, 146; *Repts. of the Newton Rigg Farm*, 1911–16. E. J. Russell, *J.*, 1917, **36**, 250–261.

Cyanamide is somewhat less effective than calcium nitrate per unit of nitrogen; but it has the compensating advantage that it is a fine powder, does not readily become hygroscopic, and can be mixed with other fertilisers to make "compounds." But it tends to contain dicyanodiamide, which is toxic to plants.[19] An important investigation by Cowie[20] has shown that the dicyanodiamide is also toxic to nitrifying organisms, and that it prevents the decomposition of the cyanamide going further than the ammonia stage. Hence it not only brings about direct injury to the crop, but has the further disadvantage of causing the crop to be fed with ammonia instead of nitrates, usually the more efficient food. This investigation has cleared up many of the observed discrepancies, and has added materially to our knowledge of the use of cyanamide. The cause of the occurrence of dicyanodiamide in cyanamide is known, and analytical methods have been devised for estimating the amount present;[21] one may reasonably hope that it will sooner or later be eliminated.

Attempts have also been made to introduce two new synthetical nitrogen fertilisers.

In view of the large stocks of ammonium nitrate that will be in existence at the end of the war, numerous attempts have been made to utilise it as a fertiliser. It has obvious advantages. It contains a considerably higher percentage of nitrogen than the substances ordinarily in use—35%, instead of 20% in ammonium sulphate, and 16% in sodium nitrate—a great consideration in matters of transport. On the other hand, the older material was highly deliquescent, so that it could not readily be stored on a farm or applied with an ordinary drill. Under relatively dry conditions it proved less effective than sodium nitrate or calcium nitrate: in damper conditons in Scotland, however, it has proved equally effective with them.[22] A modification is now obtainable which is far less deliquescent, and can readily be drilled.

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[18] Norsk Hydro-Elekt. Kvaelstofaktieselskab, Eng. Pat. 114873; *J.*, 1918, 315A.

[19] T. Pfeiffer and W. Simmermacher, *Landw. Versuchs-Stat.*, 1917, 90, 415; *J.*, 1918, 67A.

[20] G. A. Cowie, *J. Agric. Sci.*, 1918, 9, 113.

[21] *E.g.* H. Kappen, *Z. angew. Chem.*, 1918, 31, 31. A. van Haaren, *ibid.*, 129-131; *J.*, 1918, 478A.

[22] *Rothamsted Rept.* for 1914, p. 42. E. J. Russell, *J.*, 1917, 250. J. Hendrick, *J.*, 1918, 146. T. Schloesing fils, *Comptes rend.*, 1918, 166, 714; *J.*, 1918, 344A.

From patents that have been taken out it may be inferred that in Germany efforts have been made to prepare urea from cyanamide and use it as fertiliser. It would have the advantage of high concentration—46·7% of nitrogen—and would thus be by far the richest fertiliser on the market.[23]

Whether these two substances—ammonium nitrate and urea—prove useful in agriculture or not, it is certain that there is a great future for synthetical nitrogenous fertilisers. The United States has arranged for great developments of the industry,[24] as also has Japan.[25]

One of the most important problems presented to the technical chemist is the evaluation of nitrogen compounds for fertiliser purposes. Unfortunately, no really satisfactory analytical method has been devised, the various processes—such as the Street permanganate method—all involving the assumption that substances decomposable in the laboratory in a certain order will decompose in the same order in the soil. The only safe method is to make pot experiments, which, unfortunately, are lengthy and tedious.[26] An important series, extending over twenty years, has just been concluded by J. G. Lipman[27] of the New Jersey Experimental Station, with the following results:

	Relative availability.	Nitrogen recovered in crop per cent.
Sodium nitrate	100	62·4
Ammonium sulphate	76	47·5
Dried blood	62	38·7
Farm-yard manure	52	32·7

In English experience these fertilisers come out in the same order, but usually with less difference between ammonium sulphate and sodium nitrate.

Phosphatic fertilisers have come in for a considerable amount of investigation. At one period of the war the shortage of sulphuric acid was a source of anxiety to superphosphate manufacturers, and efforts were made to use nitre-cake in partial replacement of the acid. Chemically, the substitution is quite feasible; in practice, however, it leads to difficulty, because the nitre-cake superphosphate tends to set to a hard mass in the den, thereby prolonging the excavation. The difficulty was diminished by curtailing the time during which the mixture is left in the den and reducing the amount of water used; under proper conditions a merchantable product resulted. Broadly speaking, too much water led to mechanical difficulties, and too little water to insufficient interaction and therefore incomplete utilisation of the rock phosphate. Agricultural trials showed that the nitre-cake superphosphate is as useful as ordinary superphosphate when the comparison is made on the basis of equal amounts of phosphoric acid.[28]

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[23] Ger. Pat. 285259; *J.*, 1915, 1116. U.S. Pat. 1275276; *J.*, 1918, 666A. Ger. Pat. 304184; *J.*, 1918, 385A.

[24] *J.*, 1918, 299R.

[25] *J.*, 1918, 320R.

[26] E. J. Russell, *J.*, 1918, 45R.

[27] J. G. Lipman and W. A. Blair, *Soil Sci.*, 1918, 5, 291; *J.*, 1918, 521A.

In addition, other methods were suggested for dissolving the phosphate in rock phosphate. In the United States, rock phosphate was added to fermenting farm-yard manure in the hope that the acids liberated would dissolve it. This proved illusory; but a certain degree of success was attained when sulphur was added: the sulphur apparently was oxidised and the resulting acid attacked the phosphate.[29]

In this country, fermenting peat was suggested;[30] in Italy[31] and South Africa, heat.[32]

Basic slag, being a home product, assumed great importance during the war. A great change, however, has occurred in its manufacture which profoundly affects its composition. Prior to the war, the slag with which the agriculturist was familiar was made in the Bessemer converter.[33] It was to the steel-makers' interest to make a rich slag. Phosphorus was needed in pig-iron because it helped in attaining the necessary temperature in the converter: as a natural consequence the slag was rich in phosphorus. But with the coming of the basic open-hearth process the Bessemer converter seems doomed; in this new process it is not to the interest of the steel-maker, but against his interest, that the pig-iron should contain phosphorus. Hence the old practice of enriching pig-iron in phosphorus in the blast-furnace is going out, and the new slags instead of 40% of phosphates contain only 20–30%. Worse still from the point of view of the analyst, in order to remove sulphur in the open hearth it is necessary to add a fair amount of lime; but this lowers the fusibility of the slag. Calcium fluoride is therefore added to increase the fusibility; unfortunately, however, it lowers the solubility of the slag in citric acid, the solvent widely used for purposes of evaluation. Thus the old Bessemer slags would contain some 40% of phosphate, 85 or 90% of which was soluble in 2% citric acid, while the modern open-hearth slag contains 20 or 30% of phosphate, only 30 to 50% of which is soluble in citric acid.

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[28] E. J. Russell, *Report on Nitre-Cake and Superphosphate*, H.M. Stationery Office, 1918. See also *Fifty-Fourth Rept. of Alkali Works Inspector*, 1917; *J.*, 1918 522A. Also J. A. Voelcker, *J. Roy. Agric. Soc.*, 1917, **78**, 242.

[29] H. C. McLean, *Soil Sci.*, 1918, **5**, 251; *J.*, 1918, 521A.

[30] Eng. Pats. 20788, 20789 of 1914; *J.*, 1915, 625, and 1157.

[31] *J.*, 1918, 437R.

[32] A. M. Johnstone, *J. Chem. Met. Min. Soc. S. Africa*, 1917, **18**, 140; *J.*, 1918, 132A.

[33] A curious error has crept into some of the agricultural text-books and lecture notes, and turns up frequently in candidates' examination papers. It is stated that basic slag is the *lining* of the Bessemer converter. This, of course, is not the case: the material is a true slag.

Two methods of approaching the problem have been adopted. Attempts have been made to enrich the open-hearth slag either by direct addition of mineral phosphate or by fractionating the slag—pouring it off in two lots instead of one. Attempts have also been made to show that the falling off from the old standard is not so serious as it looks, it being claimed that the citric-acid test is not so important as was previously supposed.

Naturally, enrichment would be the more useful to agriculturists if it were practicable. Of the methods proposed, direct addition of mineral phosphate to the slag is not generally considered legitimate unless it could be done so as to alter the mineral phosphate and make it more like slag in composition and properties.[34] Now the steel-makers would not care to have mineral phosphate added in the furnace, and it is not clear that additions made to the slag in the ladle would have any effect. This problem certainly needs fuller investigation. The fractionation method is more immediately promising: by the preliminary use of a "mixer," or by the Hoersch process,[35] it is possible to separate the slag into two or more fractions, the higher of which may contain as much as 36% of phosphates, 80% of which is soluble in 2% citric acid, while the lower fractions contain much less.

Besides these attempts to improve the open-hearth slag, some vigorous apologists have appeared for the slag as it stands. G. S. Robertson has made a trenchant attack on the conventional citric-acid test and roundly declares it to be worthless as an index of fertiliser value.[36] Gilchrist and Louis [37] also support this view. On the other hand, the Agricultural Educational Association—a body that includes most of the agricultural experts of the country—has arranged co-operative tests, from which it concludes that the citric-acid test justifies its retention.[38] Oldershaw's field experiments also lead to this conclusion.[39] Perhaps the fairest conclusion from the available data is that high solubility is desirable where the growing-season is short, but less important where it is long.[40]

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[34] It should be noted that basic slag is probably a silico-phosphate: at any rate, it differs from ordinary mineral phosphate.

[35] See also B. Queling, Ger. Pat. 304894; *J.*, 1918, 428A.

[36] G. S. Robertson, *J. Bd. Agric.*, 1918, **24**, 1077; *J.*, 1918, 132A.

[37] D. A. Gilchrist and H. Louis, *J.*, 1917, 261.

[38] Private communication, Agricultural Education Association.

[39] A. W. Oldershaw, *J. Bd. Agric.*, 1917, **24**, 819; *J.*, 1918, 15A.

Robertson and Gilchrist have gone still further and have investigated the conditions under which rock phosphate itself could be used as fertiliser. In general it is found to act well, especially when very finely ground. Indeed, with further improvements in the mills, rock phosphate, under suitable soil and climatic conditions, might prove almost as effective as bone-meal or even slag. American experience also justifies this view: rock phosphate is effective, but slower in action than superphosphate; each farmer must therefore decide which is the more economical fertiliser for him to use.[41] In anticipation of useful results from rock phosphate, efforts have been made to concentrate low-grade material by calcination and subsequent levigation.[42]

A new phosphatic fertiliser has been prepared in the United States—an ammonium phosphate sold as "Ammophos." The method of preparation is said [43] to be as follows: ground rock phosphate is mixed with sufficient sulphuric acid to ensure liberation of phosphoric acid, which is then removed by filtration and washing the residue. Gaseous ammonia, produced by steaming crude cyanamide in an autoclave under several atmospheres' pressure, is bubbled into the acid till it is converted chiefly into diammonium phosphate, when more phosphoric acid is run in till the monophosphate is formed. The solution on evaporation yields a light grey powder containing 13·5 % of ammonia and 43·1% of phosphoric oxide (P_2O_5), *i.e.* two-thirds as much nitrogen as sodium nitrate, and three times as much phosphoric acid as ordinary superphosphate.

Potassic fertilisers have never played as prominent a part in British agriculture as nitrogen compounds or phosphates, but they are necessary for starch- and sugar-forming crop such as potatoes and mangolds and also for flax. At the outbreak of the war there was a search for substitutes, which, fortunately, was not hurried, as supplies in this country were sufficient to last for a time. The most hopeful source is dust from blast-furnace flue-gases,[44] which is collected in a mechanical catcher, or, better still, precipitated from the gas by electrostatic means.[45] Since the gases are used for firing stoves and boilers, it is an obvious advantage that they should be free from dust: indeed, the gain is said to outweigh the expense, so that the dust really costs nothing to produce. Its potash content varies from 3 to 15% of K_2O; [46] sometimes, however, cyanides and thiocyanates are also present. The dust itself has been used as a fertiliser in emergencies with satisfactory results, but it has numerous disadvantages. The more permanent method of lixiviation and evaporation has therefore been adopted, yielding a potassium chloride or sulphate of any desired degree of purity.[47] The process is actually at work in Lincolnshire and other English furnace districts and is considered by its supporters to be a permanent addition to British industries. Data are furnished by Berry and MacArthur as to the prospects of founding a similar industry in Scotland.[48]

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[40] E. J. Russell, *Manuring for Higher Crop Production*, Camb. Univ. Press, 1917, p. 35.

[41] W. H. Waggaman and C. R. Wagner, *J. Ind. Eng. Chem.*, 1918, **10**, 442; *J.*, 1918, 478A.

[42] H. A. Webster, U.S. Pat. 1266730; *J.*, 1918, 556A.

[43] F. E. Allison, *Soil Sci.*, 1918, **5**, 1; *J.*, 1918, 252A.

[44] The first published account in this country was by H. T. Cranfield, *J. Bd. Agric.*, 1917, **24**, 526; *J.*, 1917, 1006; but, as usual, a considerable amount of work had been done by various firms before this date. H. Louis had found potash in flue-dust as far back as 1878.

The richness of the dust in potash is enhanced when salt is added to the charge in the blast-furnace, and this apparently can be done without injury to the linings or adverse effect on the "burden," with which no furnace-manager likes any tampering. The amount of potassic fertiliser used annually in the United Kingdom prior to the war contained 22,000 tons of potash (K_2O). It is estimated that 200,000 tons of potash (K_2O) is annually fed into the blast-furnaces of this country, of which one quarter ordinarily volatilises; this proportion is increased, however, if salt is added. In other words, the blast-furnace gases already contain 50,000 tons of potash per annum, and would contain more if salt were used.[49] It is further estimated that during the current season flue-dust will yield 15,000 tons of potash. At the present time the resulting 80% muriate is being sold to farmers at £32 10*s.* per ton delivered in bags. As fertiliser it is satisfactory so long as it does not contain too much toxic material.

Attempts have been made to prepare potassium salts from wool, from cement-kiln flue-gases, and also from sea-water, but no substantial contribution to our supplies has come from these sources.[50]

Various natural sources of potash have been exploited. The most important are the deposits of the Western States, especially Nebraska. This State alone is now producing salts, containing 25% of potash (K_2O), at the rate of 32,000 tons of potash per annum; whilst in 1916 the total output from the whole of the United States was only 9720 tons.[51] A similar lake has been found in Saskatchewan,[52] thirty miles north of Maple Creek. Deposits also occur in Chile. Coming nearer home, there are notable deposits in Alsace:[53] to the north-west of Mulhouse lies a tract of seven square miles in extent, estimated to contain 300,000,000 tons of potash, which it is claimed could be won at the rate of 800,000 tons per annum without incurring great expenditure. Deposits also occur in Erythrea[54] and in Spain: the latter are to be brought under stringent Government control to prevent suppression by hostile interests.[55] Other deposits occur in Abyssinia; while the possible presence of potash in this country appears not to be excluded.[56] When all these sources are fully working it may be doubted whether the Stassfurt export trade will rise from the 1·3 million 'double cwt.' of K_2O, at which it stood during the war, to the five million 'double cwt.,' at which it stood before the war.[57]

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[45] Described fully by H. J. Bush, *J.*, 1918, 389R. For other methods, see C. Heine, Ger. Pat. 302973; and G. A. Krause, Ger. Pat. 303078; *J.*, 1918, 400A.

[46] *J. Bd. Agric.*, 1917, **24**, 852.

[47] K. M. Chance, *J.*, 1918, 222T.

[48] *J.*, 1918, 1T.

[49] K. M. Chance, Cleveland Inst. Eng., Jan. 15, 1918. For American estimates, see L. Bradley, *J. Ind. Eng. Chem.*, 1918, **10**, 832–844; *J.*, 1918, 653A.

[50] For production from wool, see R. S. Weston, *J.*, 1918, 17T. Production from cement, W. H. Ross and A. R. Merz, *J. Ind. Eng. Chem.*, 1917, **9**, 1035; *J.*, 1918, 9A. From sea-water, J. H. Hildebrand, *J. Ind. Eng. Chem.*, 1918, **10**, 96; *J.*, 1918, 180A.

The possibility of new openings after the war for the fertiliser trade has been studied by a departmental committee, whose report is somewhat guarded.[58] At the same time it does not seem possible to take a depressing view of the future.[59] W. A. Davis has shown that the indigo soils of Bihar are greatly in need of phosphate. A committee has gone into the question whether this is generally true of Indian soils, and concludes on the whole that it is not.[60]

A considerable amount of interest has been taken in the use of other substances as fertilisers. Large quantities of waste lime are available, and these, when dry enough to be handled and transported, are of considerable value. Calcium sulphate, however, appears to be of less general use and no great opening has been found. Prior to the introduction of superphosphate it was much in demand, but superphosphate appears to contain all that is necessary for British agriculture. The old question whether gypsum increases the solubility of potash in soils has been re-examined by McMiller,[61] who found no noteworthy increases even under favourable conditions. This agrees with the results of the Rothamsted field-trials, which afford no evidence of increased availability of potash when the soil is treated with superphosphate containing large amounts of gypsum.[62] In some circumstances sulphates are of fertilising value, as has already been shown in this country by Dymond and others; but sufficient to meet the needs of crops is ordinarily contained in the ammonium or potassium sulphate and the superphosphate already applied.

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[51] E. E. Thum, *Met. and Chem. Eng.*, 1917, **17**, 693; A. de Ropp, *J. Ind. Eng. Chem.*, 1918, **10**, 844; J. W. Hornsey, *J. Ind. Eng. Chem.*, 1918, **10**, 832; *J.*, 1918, 87A.

[52] *J.*, 1918, 378R.

[53] *J.*, 1918, 227R; P. Kestner, *J.*, 1918, 291T.

[54] *Atti R. Accad. Lincei*, 1918, **27**, I., 331; *J.*, 1918, 689A.

[55] *J.*, 1918, 379R.

[56] *J.*, 1918, 313R.

[57] Data from *Z. angew. Chem.*, July 26, 1918; *J.*, 1918, 364R.

[58] Cd. 8994, 1918.

[59] See *e.g.* E. J. Russell, *J.*, 1917, 250.

[60] *Agr. Research Inst. Pusa, Bull.* 81, 1918.

Sodium sulphate is not without value, though it is doubtful whether farmers ought to pay for it. Sodium chloride is distinctly useful, especially for the mangold (originally a seaside plant) and for corn in chalk districts. Other and more costly substances are investigated at Woburn by J. A. Voelcker in the Hills pot experiments, reports of which are published annually in the "Journal of the Royal Agricultural Society." The subject has also been reviewed in the United States by Robinson and others,[63] who found lithium always, rubidium generally, and cæsium occasionally, present in crops. Chromium and vanadium were only occasionally found and then only in traces; tungsten was never found.

An old question, the use of manganese salts as fertiliser, has been revived. Hiltner and Korff[64] claim to have obtained positive results on soils rich in organic matter such as peats. Field experiments in this country have proved unsuccessful.

The effect of magnesium compounds has been studied in some detail, and is of interest because of the importance of magnesian limestone as a source of agricultural lime. J. A. Voelcker's pot experiments at Woburn[65] showed that magnesium oxide and carbonate increased the crop and in certain concentrations affected the grain. Other magnesium compounds—the chloride and sulphate—gave increases in crop also up to a certain point. Magnesium carbonate has no ill effect on soil bacteria, indeed, rather the contrary.[66]

In water-cultures, magnesium carbonate is found markedly injurious to plant-growth, causing a reduction in number and size of rootlets, brown or black colour of roots and rootlets, a reduction in the number of absorbent hairs and in the length of the aerial portion.[67] There are, however, important differences between water-cultures and soils, and it not infrequently happens that toxic effects are produced in water-cultures which are not shown in the soil. Reverting to the practical problem, until there is more information available the safest rule is probably to restrict the use of lime from magnesian limestone to heavy soils where in ordinary experience it does good, and to refrain from using it on light soils where injury has resulted.[68]

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[61] P. R. McMiller, *J. Agric. Res.*, 1918, **14**, 61; *J.*, 1918, 555A.

[62] E. J. Russell, '*Soil Conditions and Plant Growth*,' Longmans, 1917, p. 85.

[63] W. O. Robinson, L. A. Steinkoenig, and C. F. Miller, *U.S. Dept. Agric.*, *Bull.* 600, 1917; *J.*, 1918, 66A.

[64] *Bied. Zentr.*, 1918, **47**, 15; *J.*, 1918, 159A.

[65] *J. Roy. Agric. Soc.*, 1916, **77**, 260; *J.*, 1918, 479A.

[66] H. L. Fulmer, *J. Agric. Research*, 1918, **12**, 463; *J.*, 1918, 252A.

SOILS.

The investigations offering the most interest to the chemist have perhaps been those on the acidity of soil. It has long been known that certain infertile soils are acid to litmus paper, and also that this infertility is remedied by dressings of lime. So clearly is this fact recognised that analysts not only test soils for acidity, but even go further and ascertain what reserve of calcium carbonate is present in neutral or alkaline soils. When the soil is acid it is now usual to attempt an expression of the degree of acidity, and this is done by two types of methods:

1. Direct determination is made of the amount of calcium hydroxide or bicarbonate necessary to saturate the soil so that any further addition would leave an excess of unchanged calcium compound. This is called the lime requirement of the soil.

2. The hydrogen-ion concentration (the so-called P_H) is determined by direct electrical measurement, or indirectly by a titration method using a range of coloured indicators, or by measuring the rate of hydrolysis of sugar solution.[69]

In the case of a simple acid—such as sulphuric acid—the two methods would give concordant results. In the soil, however, they do not. It is not yet possible to account fully for the discrepancy. It is not certain that the methods of measuring the hydrogen-ion concentration applicable to a simple acid would hold in such a complex system as a soil. On the other hand, the amount of lime or bicarbonate withdrawn from solution is not simply a measure of acidity, but is affected by the adsorption capacity of the soil. At the moment, perhaps, the safest plan for the analyst in dealing with an acid soil is to determine the lime requirement, either by the Veitch (calcium oxide) or the Hutchinson (calcium bicarbonate) method, and to advise larger or smaller dressings according as the result comes out high or low.

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[67] H. Coupin, *Comptes rend.*, 1918, 166, 1006; *J.*, 1918, 479A.

[68] J. A. Hanley, *J.*, 1918, 185T.

[69] F. E. Rice and S. Osugi, *Soil Sci.*, 1918, 5, 333; *J.*, 1918, 666A. J. K. Plummer, *J. Agric. Res.*, 1918, 12, 19; *J.*, 1918, 159A. J. L. Gillespie and L. E. Wise, *J. Amer. Chem. Soc.*, 1918, 40, 796; *J.*, 1918, 384A.

In the region of soil biology, the most interesting developments have been the steady increase of knowledge of soil protozoa and the increased recognition of the part played by fungi in soil processes. Unfortunately, no English mycologist has attacked the subject with the thoroughness it deserves, and we are dependent for our information on the American workers.

A further subject that has recently attracted attention is the sulphur cycle in soils. Plant-residues, farm-yard manure and similar substances, contain sulphur in the form of very complex organic compounds; these are decomposed in the soil, giving ultimately sulphuric acid, so that they appear as sulphates. The process has received the somewhat unhappy name of "sulphofication" in analogy with "nitrification." Not only are complex sulphur compounds oxidised, but the element itself oxidises in soil. A case has been recorded by C. B. Lipman,[70] in California, of a soil markedly deficient in organic matter, and therefore not supporting an active "sulphofying" flora, on which ammonium sulphate gave better fertiliser results than sodium nitrate, which was attributed to the lack of sulphur in the latter case. When this was made good by adding sodium sulphate to the nitrate the results obtained were approximately equal to those yielded by ammonium sulphate.

It has long been known to plant physiologists that a certain balance had to be maintained between the various constituents of a nutrient solution. Thus a plant provided with all the elements necessary for nutrition might fail to give satisfactory results unless the proper proportions were observed. Several interesting papers have appeared describing in detail the injury caused when single substances—such as monobasic calcium phosphate or ammonium sulphate—are present in excess of the proper quantities.[71] To the agricultural chemist the interest of the investigation lies in the possibility that physiological balance might be a factor in soil fertility.

FEEDING-STUFFS.

During the war the most interesting work on feeding-stuffs was the search for substitutes carried out in various countries affected by the blockade. The most important of these has been a substance prepared in Germany by digesting straw with dilute caustic soda solution. The material is said to be eaten by animals more readily and to be more digestible than ordinary untreated straw; considerable claims have been made for it, and its manufacture is said to have become an important industry. Wood pulp has been utilised as fodder in Sweden. It is mixed with molasses and protein compounds, and is said to be nutritious: the output this year is expected to be 20,000 tons.[72] Of lesser substitutes, heather has received much attention: in Germany it was considered equal in value to poor quality hay if the leaves and flowers only were utilised.[73] In Denmark it was ground to a flour, mixed with blood from abattoirs, and then used as cattle food in place of oats. The results are said to be sufficiently good to justify the view that the industry may be established on a permanent basis.[74] In Sweden also, heather has been found useful. Leaves of trees—beech, maple, lime, alder, chestnut, birch—have proved useful where they could be obtained; they contain some 10–23% of protein and 2–10% of fat, but also 17–22% of crude fibre.[75] Reindeer moss, however, was of little value.

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[70] C. B. Lipman and W. F. Gericke, *Soil Sci.*, 1918, 5, 81; *J.*, 1918, 252A.

[71] J. W. Shive, *Soil Sci.*, 1918, 5, 87 (monocalcic phosphate). M. I. Wolkoff, *Soil Sci.*, 1918, 5, 123 (ammonium sulphate); *J.*, 1918, 253A.

Agricultural chemists who remember the trouble that used to be caused by the feeding of cotton-seed meal to animals, will learn with much interest that the toxic substance appears to have been tracked down. Formerly it was supposed to be choline or betaine: it proves to be something much more complex. Withers and Carruth[76] have extracted from raw cotton-seed kernels a substance of the formula $C_{30}H_{28}O_9$, to which they give the name gossypol. It is highly toxic to rats; the residual meal from which it has been removed is non-toxic. It is soluble in ether, but yields an insoluble aniline compound by means of which it can be isolated. It is also somewhat oxidisable on cooking, so that cotton-seed meal is less toxic than the raw cotton-seed. However, this is not the whole story, for apart from the presence of this toxic substance a diet of cotton-seed meal and maize meal has nutritive limitations which, under the restricted conditions of an indoor life, caused pigs not to thrive.

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[72] *Bd. of Trade J.*, Jan. 24, 1918; *J.*, 1918, 76R.

[73] F. Honcamp and E. Blanck, *Landw. Versuchs Stat.*, 1918, 91, 223; *J.*, 1918, 527A.

[74] *U.S. Cons. Rept.*, May 21, 1918; *J.*, 1918, 301R.

[75] F. Honcamp and E. Blanck, *Landw. Versuchs Stat.*, 1918, 91, 291; *J.*, 1918, 527A.

[76] W. A. Withers and F. E. Carruth, *J. Agric. Res.*, 1918, 12, 83; *J.*, 1918, 164A.

FERMENTATION AND ALLIED PROBLEMS.

Silage is a fermentation product of great agricultural importance. Green fodder—such as maize in America, or mixed oats and tares, grass, &c. in this country—is cut up and carried or blown into a large cylindrical wooden structure, known as a silo. Acetic acid is speedily produced, which acts as a preservative; so long as there is no over-development of mould, cattle eat the material with relish in spite of its odour. Silage is very popular in America, and an extension of the process has recently been suggested for converting into silage the dry stalks left after the removal of the grain.[77] The material is cut up and put into the silo, then the requisite amount of water is added; a normal silage is produced of the customary appearance and aroma, which is well relished by cattle. Unfortunately the investigators were not able to decide whether the changes are due to respiration or bacteria.

One of the most troublesome of the minor problems of the agricultural chemist relates to the spontaneous ignition of haystacks—a phenomenon which assumes practical importance in connection with fire-insurance claims. Spontaneous ignition is likely to occur when a haystack is put up too quickly and before the hay is properly "made"; the temperature rises rapidly, and eventually the stack becomes so hot that it actually takes fire. This is particularly liable to occur when farmers for any reason are anxious to get the work over. It is said in Switzerland to have become more frequent of late years, owing to the introduction of modern mechanical appliances and the consequent temptation to rush the work. The usual explanation[78] is that a rise to about 40° C. may result from respiration of the surviving plant-cells, and a further rise to about 70° C. from the activity of micro-organisms. A process of dry distillation is then supposed to set in yielding combustible gas and carbon; but the carbon is pyrophoric, owing to the fibrous nature of the original material. A different explanation is put forward by Tschirch.[79] He supposes that the first phase of heating is due to oxidation processes under the influence of the plant oxidases and at the expense of the air present in the stack. This phase results in a small rise of temperature, but ceases when the oxygen in the stack has been exhausted. After this, the chief rôle is played by reductases, which act between 50° and 70° C. and effect the oxidation and carbonisation of the amino-acids, carbohydrates, &c. There is thus a withdrawal of oxygen from the hay constituents;

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[77] J. M. Sherman and S. I. Bechdel, *J. Agric. Res.*, 1918, **12**, 589.

[78] See *e.g.* E. Jordi, *Schweiz. Chem.-Zeit.*, 1918, **2**, 7; *J.*, 1918, 190A.

[79] A. Tschirch, *Schweiz. Chem.-Zeit.*, 1918, **2**, 10; *J.*, 1918, 190A.

this is supposed to accumulate and lead to ignition. Unfortunately, neither hypothesis helps us to devise methods of remedying the trouble or to suggest any improvement on the usual practice of pulling the stack to pieces as soon as trouble is threatened; nor do the hypotheses suggest any certain way by which an analyst could determine in a particular case whether ignition had been spontaneous or caused by human agency.

The changes occurring during the ripening of cheese are known to be of biological origin. Various kinds of hard cheese—such as Cheddar and Emmentaler or Swiss—depend on suitable bacterial flora for proper development; while cheeses mottled with mould—such as Gorgonzola and Stilton—require the appropriate fungi also. Miss Evans[80] shows that in Roquefort cheese two organisms are required: *Streptococcus lacticus*, which decomposes lactose with formation of lactic acid, and the mould *Pencillium roqueforti*. The lactic acid is necessary to bring the curd into the proper physical condition. In point of fact numbers of other organisms were also present in the samples investigated, but they appeared to be unessential. Miss Evans further extends the list of activities of the streptococci. Hitherto three main groups have been recognised: (1) pathogenic; (2) those in the udder, saliva, and intestines; (3) milk souring. To this a fourth rôle is added: the formation of flavours in food prepared for consumption by fermentation, particularly cheese.

HUMAN FOODS.

In general, human foods do not come within the purview of the agricultural chemist. So far as he touches the subject his function is simply to see that the agriculturist provides the market with whatever is wanted and conforms to the standards expected there. Two papers deserving attention have recently been published, however. One deals with the strength of flour. It is well known that certain wheats—especially Red Fife and its descendants—give a large, well-shaped loaf, while others—notably Rivetts—give a small squat-looking loaf. The former are called "strong" and the latter "weak" flours. Many investigations have been made into the cause of "strength," the most important of which in this country are those of T. B. Wood, who concluded that the size of the loaf is regulated by the amount of fermentable sugar present, while shapeliness is determined by the physical properties of the gluten, which in turn depend on the amount of acids or salts present. Gortner and Doherty[81] controvert the implied assumption that the gluten is the same chemical unit in strong and weak flours. They suppose that there are several glutens. Weak glutens are supposed on an average to be nearer the boundary-line separating the crystalloid from the colloid state than are the strong glutens.

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[80] Alice C. Evans, *J. Agric., Res.* 1918, **13**, 225. These results in the main, confirm those of C. Thom, *U.S. Dept. Agric. Bureau Animal Industry, Bull.* 82, 1906.

B. T. P. Barker,[82] of the Fruit and Cider Institute, has found a solution of the problem of utilising the excess of cider apples, which is of considerable practical importance. Of the three classes of apple, the "sours" can be used for dessert or cooking purposes, and they readily yield a jelly. The "sweets" and "bitter sweets," on the other hand, have hitherto proved unsuitable for jelly-making, and have no other use except for cider; in two years of heavy crops—such as 1914—therefore, thousands of tons are wasted and their 10% or more of sugar is lost. Fortunately, Barker has been able to discover the proper conditions for preparing a jelly from them. The juice is first extracted, and is then concentrated in a Kestner evaporator till the malic acid constitutes between 1 and 1·5% of the whole; then sugar is added till the total quantity amounts to 6·5%. In practice a certain amount of blending of juice is desirable so as to ensure that the proper concentration of malic acid shall be readily obtained. It is, of course, possible to obviate any addition of sugar by carrying the evaporation far enough: in this case it would have to go to one-seventh of the original volume of the juice, the average sugar-content of which is about 10%. On the whole, it is found cheaper to add the sugar.

INSECTICIDES AND FUNGICIDES.

Until recently, chemists have confined themselves to improvements in methods of making and using insecticides. A new field of work is, however, opening out: attempts are being made to find a relationship between chemical constitution and insecticidal or fungicidal properties. From the standpoint of human physiology and pharmacology, the problem is already an old one,[83] and has yielded interesting and important results. Insecticidal work on these broad lines is being carried out at Rothamsted. Moore and Graham have made some pioneering researches into the physical properties governing the efficacy of contact insecticides.[84] Two groups of insecticides are distinguished—those which can spread over the body of the insect and penetrate the tracheæ, and those which do not. The former are usually soluble in ether or chloroform, or are fat solvents. High volatility is not desirable; compounds more volatile than xylene evaporate too quickly to be effective. Indeed, toxicity seemed to increase with decreasing volatility. Liquids which are not sufficiently volatile to kill insects or eggs exposed to their vapours were among the most toxic substances when applied as liquids. Using different fractions of kerosene,[85] the least volatile fractions were found to be the most effective as contact insecticides.

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[81] R. A. Gortner and E. H. Doherty, *J. Agric. Res.*, 1918, 13, 389; *J.*, 1918, 482A.

[82] *J.*, 1918, 37, 234T. *Annual Rept. Agric. and Hort. Research Expt. Stat., National Fruit and Cider Inst., Long Ashton, Bristol*, 1917.

[83] See the interesting summary in Pyman's lecture before the Chemical Society.

[84] W. Moore and S. A. Graham, *J. Agric. Res.*, 1918, 12, 579, and 13, 523; *J.*, 1918, 280A, 484A.

A promising new poison has been found in the tropical or subtropical plant *Derris elliptica*, which produces general motor paralysis in fishes, frogs, and mammals, and no doubt would prove effective in other cases. The toxin is said to be tubatoxin, $C_{18}H_{18}O_{15}$, which is soluble in most organic solvents, but not in water, acids, or alkalis: it forms white crystals from alcohol and reduces ammoniacal silver and copper solutions.[86]

The suggestion has also been made to use calcium arsenate, in place of lead arsenate, as a spray. The advantage would be that lead would thus be eliminated, and there would be no danger of the presence of water-soluble arsenates, which might burn the foliage.[87]

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[85] *J. Econ. Entom.*, 1918, **11**, 70.

[86] *Jap. Med. Lit.*, 1917, **1**, 7; *J. Chem. Soc.*, 1918, i. 94.

[87] R. H. Robinson, *J. Agric. Res.*, 1918, **13**, 261; *J.*, 1918, 439A.

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By James P. Ogilvie,
Technical Editor, "International Sugar Journal," London.

Statistical.—Present-day statistics relating to the sugar industry naturally resolve themselves into a comparison between the figures for the last pre-war year and those latest available. In 1913–14 the cane sugar crop from all sources (together with that of British India, which is consumed locally, and ought, strictly speaking, not to be included) totalled 9,773,348 tons[1]; while the beet sugar production amounted to 8,850,470 tons, of which Europe accounted for 8,185,165 tons, the balance being produced by the United States and Canada. The 1917–18 estimates of Willett and Grey[2] give the world's cane sugar crop as 12,276,103 tons, and the beet sugar crop as 4,517,212 tons, of which Europe yields 3,823,095 tons. It is therefore seen that, while the supply of cane sugar has risen after four years of war by 2,502,753 tons, the beet crop has dropped by 4,333,258 tons. The most outstanding instance of increase in cane sugar production is furnished by Cuba, the output of which last season was 3,446,083 tons, as compared with 2,597,732 tons in 1913–14, but there have been marked increases in production also in Porto Rico, Peru, Brazil, Java, Formosa, and the Philippines. As for sugar production in the British Colonies, there have been appreciable percentage increases in output, but the totals are still small, and do not materially affect the world's supply. Thus Jamaica has doubled its output in the years under review, but that only means that it is now yielding 34,000 instead of 15,000 tons, while the Mauritius crop has fluctuated of late years between 200,000 and 265,000 tons. The locally consumed sugar made in British India has increased from 2,262,600 tons in 1913–14 to 3,229,000 tons, the estimate for 1917–18; but this production has practically no influence on the trend of the world's sugar market.

Turning now to the sugar supply of the United Kingdom, the influence of the war on the sources of the sugar imported is not without interest. According to the Board of Trade figures, in 1913, the last complete pre-war year, we imported 1,046,482 tons of unrefined sugars, of which Germany contributed 471,689 tons (beet), Austria, 161,038 tons (beet), and Cuba, 223,980 tons (cane). Of refined sugars we imported 924,800 tons, of which Germany's quota was 466,749 tons (beet), Holland's, 178,789 tons (beet), and Austria-Hungary's, 198,431 tons (also beet). In fact, practically the whole import of refined sugars was beet.

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[1] *Intern. Sugar J.*, 1915, 149.

[2] *Weekly Statistical Sugar Trade Journal*, 1919, 43, No. 2.

Comparing these figures with the most recent ones available, it is found that in 1916 we imported 1,126,479 tons of unrefined sugar, of which 289,465 tons (cane) was shipped from Java, 553,563 tons (cane) from Cuba, and 68,198 tons (cane) from the Philippines, together with 410,765 tons of refined (most of which came from the United States, though the quantity quoted included some 94,000 tons of plantation whites from Java). To this import the contribution of European beet was but 4350 tons, nearly all from Holland; and, apart from the possible inclusion of some American beet in the American quota, the rest of the import was cane sugar. Thus, with a consumption decreased by rather less than 25%, we have substituted cane sugar from various sources for some 1,472,000 tons of European beet sugar.

There is some prospect of extending the sugar industry in the British Colonies, and plans have been formulated in Jamaica for the erection of several Government-aided central factories; but while the war continued, and especially pending a definite declaration on the part of the British Government on the subject of imperial preference, capitalists have hesitated to embark on new schemes of any magnitude. However, the near future should see a change to activity, especially as the home electorate have to all appearances confirmed the Coalition Government's decision to give preference to imperial sugar.

SUGARS.

THE CANE SUGAR INDUSTRY.

Cultivation of the cane.—C. F. Eckart's novel and ingenious method[1] of preventing the development of weeds in the cane fields, based on the principle that, whereas the growing cane shoots are capable of piercing a covering of paper or similar material laid directly on the rows of stubble immediately after harvesting, weeds fail to penetrate and therefore wither and die, gives promise of successful results. Experiments carried out on the Olaa plantation, in Hawaii, of which the inventor is

[1] *Intern. Sugar J.*, 1917, 455; U.S. Pat. 1249355.

manager, are claimed to have demonstrated that 50–70% of the labour ordinarily expended on the cane-fields can be saved by this means;[4] and that, moreover, owing to the improved soil conditions, an increased yield of cane amounting to about 10 tons per acre is to be expected. Further tests are being carried out independently on several other estates in the Territory, and the results of these trials will be watched with more than usual interest by sugar planters, particularly those in countries where labour is expensive or is difficult to obtain. Success will largely depend upon the cost per acre of the material used for covering the cane rows, of which a large surface will be required. At Olaa a mill is being erected for the manufacture of a suitable paper for the purpose (and also, it is reported, of other papers of many grades for export), exhausted cane bagasse being utilised as the raw material.

A very thorough investigation of the comparative effect of different fertilisers in cane cultivation, which indeed might well serve as a model for tests in other places where yet there is insufficient information upon the subject, has been carried out by J. Mirasol y Jison[5] in the Philippines. He found that the highest purity of the juice was obtained with potassium sulphate either alone or else as a complete fertiliser in combination with sodium nitrate and double superphosphate; whereas its purity was lowered to a considerable extent with double superphosphate in combination with nitrogen, either in the form of ammonium sulphate or as sodium nitrate, the effect upon the percentage of the sucrose in the juice running parallel to that on the purity of the juice. Ammonium sulphate in combination with potassium sulphate, or with double superphosphate, produced the highest yield of cane, dried blood and potassium sulphate apparently having the contrary effect, though an increased yield of cane was shown not to result in a greater nett amount of commercial 96 sugar. Tests carried out with complete fertilisers indicated sodium nitrate to be far superior to ammonium sulphate as a source of nitrogen for the cane. It was concluded that under the particular conditions of the experiments the highest financial returns would be obtained with a complete fertiliser containing potassium sulphate, sodium nitrate, and double superphosphate (the nitrogen, potash, and phosphoric acid being in the ratio of 8 : 6 : 8).

Some of the results obtained by R. Narain[6] upon the rôle of the oxidases of the cane are striking. He observed that on boiling cane oxidase extracts their activity, though at first apparently destroyed, is actually only suspended temporarily, and gradually returns to its original value, there being a recovery even after boiling twice. Further, it was possible to obtain the guaiacum reaction from extracts of cane leaves which had been dried at 100° C. during six hours, while even the ash of these leaves gave a faint but distinct indication with the same reagent. In view of these results, it would seem impossible longer to regard oxidases (or at any rate the substances present in cane believed to be such) as enzymes, or else conceptions regarding them must be changed. Other experiments of this author showed cane oxidases to be extremely sensitive to the reaction of the medium, their activity diminishing as the acidity of the extract increases. It appears that their activity in the growing plant may be controlled by variations in the acidity of the sap, since it was found both in unripe and in fully developed cane that the acidity of the sap is distinctly lower in the afternoon, when the sun is strongest, and other photosynthetic processes are in progress, than in the earlier part of the day. As one would anticipate from our knowledge of the requirements of the plant, it was found that the oxidases are more active in the upper part of the stem than in the lower; in the rind than in the pith; in the nodes than in the internodes; and, finally, in the open flat part of the leaf than in the sheath or curled-up portion.

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[4] *Intern. Sugar J.*, 1918, 567.

[5] *Philippine J. Sci.*, 1918, A, 13, 135; *J.*, 1918, 632A.

[6] *Agric. J. India (Special Science Congress Number)*, 1918, 47; *J.*, 1918, 632A.

Extraction of the juice by milling.—Great progress in milling has been made during the past few years in Hawaii, and by means of recent improvements the extraction in some factories has reached the high figure of 97–98% of the sugar present in the cane. This has been accomplished, not only by increasing the number of units in the train (which now quite generally consists of four 3-roller mills and one 2-roller crusher), but also by means of grooved rollers, and devices that prepare the cane previous to crushing, as shredders and revolving knives. A better system of maceration (or extraction by water of the juice remaining in the crushed bagasse) has also helped to make possible these excellent results.

But while such innovations are of undoubted utility in increasing both the extraction and the grinding capacity of the milling plant, they are now being found to possess certain disadvantages, as several managers in whose factories they have been installed point out in a symposium on the question. Thus, G. Giacometti[7] states that the reduction of the cane by means of shredders and knives to a very fine state ultimately gives a bagasse having a fuel value inferior to that of the usual coarser material, much of it passing up the chimney in a carbonised state. T. Murray[8] shows that the purity of the extracted juice is decreased in a marked degree, and quotes figures for the past ten crops of his estate, separating those relating to an extraction of 92·2, when a 9-roller train was used, from others indicating a higher extraction more recently obtained by means of a modern 12-roller mill. In both cases the purity of the first expressed juice had been about the same, viz. 89·7 and 89·4 ; but the purity of the mixed juice was 86·8 and 84·9 respectively, and that of the last mill juice, 79·9 and 68·6 ; while the purity of the syrup was 89·2 and 87·1, and the amounts of " mud " separated after treatment with lime were 1·6 and 2·2% of the cane crushed during the two periods under comparison.

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[7] *Intern. Sugar J.*, 1918, 189.

[8] *Ibid.*, 1918, 82.

Another effect of this heavy milling, and an important one, is that a much greater amount of *bagacillo* finds its way into the juice, so that settling after the defecation treatment with lime is hindered, while these very fine particles of bagasse also pass over to the syrups and molasses, particularly after grinding soft cane, making the crystalliser massecuites more viscous, impeding the centrifuging of the low-grade products, and also probably diminishing the keeping qualities of the finished sugar during storage.[9]

Clarification of the juice.—In modern practice it is almost universal in factories using the common defecation process of purifying the juice from the mills, to treat with lime, heat, and allow to subside in settling tanks, the juice being separated by decantation and sent to the evaporators, while the " mud " may again be treated, and finally washed in filter-presses. But if the effects mentioned caused by the greatly increased amount of *bagacillo* and gummy matter in the mill juice are to be remedied, and the production of an inferior sugar is to be avoided, a more thorough separation of the suspended matter than can at present be realised by mere subsiding becomes necessary.

Certain factories in Hawaii and Cuba are therefore adopting the practice of filtering the entire clarified juice in place of the subsided muddy portion only. For this purpose, besides ordinary plate-and-frame presses, those of the Sweetland and Kelly types are being used. S. S. Peck[10] describes tests carried out in Hawaii, in which kieselguhr at the rate of 5 lb. per ton of cane was used to form a preliminary coating upon the surface of the cotton-drill cloth used in the presses ; he estimates the area necessary for the filtration of the " mud " and the subsided juice separately to be 100 and 90 sq. feet per ton of cane per hour respectively, and that required for the direct filtration of the entire juice without subsiding to be 170 sq. feet per ton of cane per hour. In another factory in the Territory, the procedure is stated by E. T. Westley[11] to be to lime to slight alkalinity, to heat to 220° F., and after settling in cylindrical tanks with cone-shaped bottoms, to pass the entire subsided juice through Gartley filters (the medium in which is bagasse), the " mud " from the tanks being passed through the presses, and the resulting juice also sent through the Gartley filters. Sometimes in other factories the subsided juice is screened through wire cloth of 100–200 meshes to the inch,[12] but this appears to be only a partially efficient means of separating the insoluble matter. Encouraging results have now been obtained after much experimental work in Hawaii and in Louisiana with centrifugal clarification, using machines designed by E. W. Kopke [13] and G. M. Newhall,[14] a system that is more rapid, occupies less space, and is more economical as regards labour than those involving the use of subsiding tanks and filter-presses. It is stated to give a juice free from *bagacillo* and gums, and it has been found [15] that by liming the cold juice to a decidedly alkaline reaction, passing it through the machine, neutralising it with sulphur dioxide and heating it to coagulate the albuminoids, a very brilliant and light-coloured juice, capable after a second filtration of producing a practically white sugar and a molasses of low viscosity, is obtained. A rather high power consumption, however, appears to be the factor that has militated against the greater success of the centrifugal clarifying machine.

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[9] *Cf.* also this Report, p. 370.

[10] *Intern. Sugar J.*, 1918, 332–333 ; *J.*, 1918, 480A.

[11] *Intern. Sugar J.*, 1918, 81.

An interesting point, worthy of note in connection with the filtration of subsided " mud," is recorded by A. Schweizer and G. Loos.[16] It had been noticed during the 1916 crop in a certain factory in Java, using the ordinary defecation process of clarification by treatment with lime, that the capacity of the Kelly presses, which had recently been installed, was not as great as had been found in houses in which defecation followed by sulphitation was being practised, the efficiency of " sweetening off " in particular being much decreased. Ascribing this to a difference in the nature of the mud, efforts were made to improve matters by the addition of different materials, such as fine carbon, but without appreciable success, since slow filtration and difficulty in dropping the mud from the frames and in cleaning the cloths still persisted. Accordingly, in order as closely as possible to imitate the conditions prevailing in the defecation-sulphitation factories, the juices were sulphited by heating the muddy juices to 80° C. and introducing lime and sulphur dioxide simultaneously, thus guarding against the danger of "glucose" decomposition at the high temperature used. The effect of this treatment was greater than was anticipated, the muddy juice passing with great ease through the filter-presses, giving hard and dry cakes. A similar procedure, it may be remarked, was to the knowledge of the present writer adopted in a certain refinery in this country having trouble with the filtration of cane liquors, which were unusually "gummy," an improved clarification and much increased rate of filtration being the result.

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[12] *Intern. Sugar J.*, 1918, 30.

[13] *Ibid.*, 1918, 29; *J.*, 1918, 160A; also U.S. Pats. 1119174 and 1119175.

[14] *La. Planter*, 1918, **60**, 87.

[15] *Intern. Sugar J.*, 1918, 289.

[16] *Archief Suikerind. Ned.-Indië*, 1917, **25**, 1561; *Intern. Sugar J.*, 1918, 39; *J.*, 1918, 160A.

Boiling to grain, curing, and finishing.—During the process of graining sugar in the vacuum pan, the temperature of evaporation is intentionally varied at different stages of the process; but notwithstanding this variation the solution must always be kept in a supersaturated state, otherwise crystallisation would be arrested or reversed. It is of importance to the operator to know at any moment the degree of supersaturation of the liquor in which graining is taking place, and an instrument has been invented by E. V. Miller and F. P. Worley,[17] which will show at a glance the refractive index of the liquid portion of the contents of the vacuum pan. Measurements have also been made by these authors of the refractive index of supersaturated solutions of sucrose with the object of determining the influence of the temperature between 30° and 75° C. and of the concentration between 72 and 81%. They found that the refractive index in its dependence upon the temperature t in degrees C., and the percentage of sucrose in solution p, can be satisfactorily represented by the equation: $r = 1{\cdot}28534 - 0{\cdot}0001241t + (0{\cdot}00263 - 0{\cdot}000001267t)p$, from which equation a table has been calculated showing the values of the refractive indices of solutions of sugar contents from 71 to 77%, and for temperatures from 110° to 170° F. By the use of the instrument mentioned, and by reference to this table, the degree of supersaturation can thus immediately be determined.

As a corollary of the theory of the formation of molasses, elaborated by H. C. Prinsen Geerligs,[18] it follows that there is an optimum water content to which the massecuite during boiling in the vacuum pan must be reduced in order to attain the maximum exhaustion possible in practice. If more water be left in the massecuite than corresponds with the real water content of the hydrated combination of sucrose, reducing sugars, and salts (of which, according to the theory, molasses is composed), the excess water retains free sucrose in solution, and the final molasses is not fully exhausted. If, on the other hand, concentration has been carried beyond the optimum point, the viscosity of the product may be so greatly increased as to retard crystallisation, rendering the work of separation very laborious. A procedure is now described in detail by Prinsen Geerligs[19] for the determination of this optimum water content of molasses; and from the values obtained, as well as from practical tests carried out in the sugar-house, it is concluded that the concentration to which molasses should be boiled to obtain a fully exhausted molasses may be about 16% of water (*i.e.*, about 84% dry substance as indicated by the refractometer), but will vary according to the composition of the sample. A final molasses at this density may contain 160–174 parts of sucrose per 100 of water, depending upon the purity of the particular product under consideration. These results are of particular value in the desaccharification of molasses in crystallisers; and it would be interesting to have data from chemists engaged in such work showing the water content by the refractometer to which their last massecuites had been evaporated to give the best results together with analyses of the final molasses obtained. In this way, the optimum water content of molasses of different constitution would be established.

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[17] *J.*, 1918, 98T.

[18] *J.*, 1895, 667; *Intern. Sugar J.*, 1918, 168; *J.*, 1918, 316A.

Manufacture of plantation white sugar.—In contrast with the past few years, little has been published during the period under review on the manufacture of white sugar on the plantation, though now there is good reason to expect that this subject will once more claim attention, particularly if the efforts to utilise decolorising carbons for refining, to which reference is made later,[20] should prove successful. The writer of this report[21] describes a trial with the Weinrich process,[22] the principle of which is that when caustic lime is added to a magma of raw sugar and juice, there is a much greater effect on the purity than when clarification is carried out with raw juice in the ordinary way. After treating with lime and twice carbonating, an almost water-white and perfectly clear juice was obtained, from which a satisfactory white sugar could be recovered on boiling. It is claimed that by this process results much superior to those obtained by the carbonatation process of clarification (as practised in Java) can be attained. Further, it enables a raw sugar factory to operate as a refinery during the usual grinding seasons, by converting its own or purchased raw sugar into white granulated without the use of additional plant.

In India good work is being done by the Government advisers in the direction of improving wasteful native methods, with the object ultimately of introducing suitable processes for the production of an improved direct-consumption sugar. At the Experimental Sugar Works, Bareilly, U.P., excellent white sugar has been made by W. Hulme[23] by sulphiting and liming the juice, subsiding and filtering it, and centrifuging and washing the resulting massecuite, the yield, moreover, being stated to be comparatively good.

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[19] *Intern. Sugar J.*, 1918, 214–218; *J.*, 1918, 385A.

[20] *Cf.* also this Report, p. 373.

[21] *Intern. Sugar J.*, 1917, 450; *J.*, 1918, 16A.

[22] U.S. Pat. 1084772; *J.*, 1914, 211.

Storage of raw sugar.—During the storage of raw sugar previous to refining, deterioration owing to the action of micro-organisms may take place under certain conditions, and the financial loss from this source must amount to a considerable sum annually. A very thorough investigation of the circumstances under which deterioration may occur has been made by C. A. Browne,[24] and his results, here briefly summarised, form a contribution of importance to those concerned with the matter. His experiments confirmed the validity of the "factor of safety" rule, suggested by the Colonial Sugar Refining Co., of Sydney, Australia, namely that the quantity $W/(100-S)$, in which W and S are the water and sucrose contents respectively of the sugar, must not be greater than 0·333. As a corollary of this rule, it follows that slight fluctuations in moisture content will have a far greater influence on high-grade than on low-grade sugars, and this is confirmed by experience in the storage of such products. A second deduction is that the displacement of moisture by non-sugars should render a questionable sugar fit for storage, a conclusion which also has been confirmed in practice, since it is customary in some factories to wash the sugars in the centrifugals with low-grade molasses instead of with water, it having been found that such sugars do not "go back" during storage under proper conditions. A mycological study of the micro-organisms present in raw sugars shows that the destruction of sucrose is not due to any single organism, or class of organisms, since moulds and budding fungi, as well as bacteria, may be expected to be present, a conclusion that has also been arrived at by W. J. T. Amons.[25] Organisms causing the inversion of sucrose in raw sugars are unable to thrive in saturated solutions, and the washing of raw sugars in the centrifugals, thereby diluting the saturated films of molasses to a point at which the organisms become active, must be regarded as a leading cause of deterioration. *Bagacillo* in raw sugars has been suspected by some as a cause of deterioration,[26] and according to Owen this impurity may retain moisture and create zones favourable for the growth of micro-organisms. Another dangerous source of infection is the cooling tower, in which condensation water from the factory is allowed to fall in a shower over a frame-work into an exposed basin, and sometimes such contaminated water is even used for washing the sugars in the centrifugals. Regarding the general means of producing sugars that will keep well on storage, it is necessary: (1) to exercise the utmost possible cleanliness and care during manufacture, in order to diminish the infection; (2) to control the moisture content of the sugar, so that the ratio of non-sucrose to water is within the limit of safety; and lastly (3) to cool the sugar thoroughly before bagging to prevent the migration of water and the formation of zones of high-moisture content.

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[23] *Intern. Sugar J.*, 1918, 236.

[24] *J. Ind. Eng. Chem.*, 1918, 10, 178; *J.*, 1918, 275A.

[25] *Intern. Sugar J.*, 1918, 40; *J.*, 1918, 160A.

[26] *Cf.* also this Report, p. 366.

It is also necessary to consider the conditions under which the sugar is warehoused—a question which during the past few months has received much attention in Java, where about 1,000,000 tons of the 1917 crop was kept during the rainy season of 1917–18 in stores of varying construction in different parts of the island. L. G. L. Steuerwald[27] observed that stores with roofs constructed of tiles gave the worst results, because this covering absorbs moisture and is non-conducting, the warmth of the sun being prevented from penetrating into the interior of the building. These two circumstances combined caused the atmosphere to have a relative humidity of about 90° during the day and to approach saturation point at night, so that, since white plantation sugar absorbs moisture from the atmosphere with a relative humidity of 84°, and refining crystals with one of 70°, the conditions were highly propitious for the rapid absorption of moisture by the product. Somewhat improved results were obtained in stores in which the roofs were of glass and in which windows were provided for suitable ventilation, but corrugated iron, on account of its heat-conducting property, proved better. Not less important than the material of which the roof is made, is the manner in which the floor is constructed. Sand on the whole proved unsatisfactory, while earthenware or tile floors, and also those of brick laid in cement, were found readily to allow moisture to pass upwards through them. After considering the data relating to the different conditions of storage, it was concluded that the best results may be expected when impermeable floors of asphalt or concrete are used, when the roofs and walls are of corrugated iron, when the bags are piled on railway sleepers covered with a thatch-work of bamboo or rattan, permitting circulation of air beneath and between them, and finally when a slow current of dry and moderately warm air is conducted through the whole length of the building.

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[27] *Archief Suikerind. Ned.-Indië*, 1918, **26**, 879; *Intern. Sugar J.*, 1918, 543; *J.*, 1919, 24A.

THE BEET SUGAR INDUSTRY.

British beet sugar.—Projects for the production of beet sugar within the United Kingdom are still in a state of suspense. The one factory existing at the outbreak of war, that at Cantley in Norfolk, had to close in 1916, owing to the adverse circumstances and to inability to obtain the necessary seed for the following crop. Plans have been laid for the inauguration after the war of a beet sugar factory at Kelham in Nottinghamshire, the British Sugar Beet Growers' Society, Ltd., being responsible for the task, while the Government are guaranteeing financial assistance and are otherwise associated with the scheme. The seed difficulty has here also delayed matters, while no buildings could be erected nor plant constructed during the time that the war continued, only preliminary work having been undertaken, consisting of clearing the estate and cultivating crops of cereals. Those responsible for this new venture have all along maintained a persistent reserve as to details or plans, but it is known that the projected factory is to be capable of dealing with at least 1000 tons of roots per day, which on the moderate estimate of 10 tons per acre would occupy about 8000 acres, producing about 80,000 tons of roots, and yielding about 11,200 tons of sugar on the basis of a content of 14%.[28] In view of the approaching return to peace conditions, it may be assumed that this scheme will be developed at an early date, the Government having promised that as soon as possible after the war the erection of the factory would be taken in hand. No other projects within the United Kingdom have so far made any progress, but if the agricultural policy of the new Coalition Government is at all favourable, there will doubtless be other attempts made to start beet factories in suitable districts, while Cantley will almost certainly resume operations before long.

Cultivation and manufacture.—Nothing has been published during the period under review of sufficient importance for note or comment under this heading, a position of affairs in striking contrast to pre-war years, when numerous interesting papers on the development of beet sugar production in France, Belgium, Holland, Germany, and Austria were the rule.

THE REFINING INDUSTRY.

Decolorising carbons.—No innovation during the past few years has aroused greater general interest in the sugar world than the effort to introduce powerful decolorising carbons, first made in the case of "Eponit" in Austria,[29] and more recently in that of "Norit" in Holland;[30] the effect of these preparations, so far as removal of colour is concerned, is at least ten times that of ordinary animal charcoal or bone-black. It is obvious that such carbons possess great possibilities. Thus, the refiner, in place of his present mode of passing the liquors through immense cisterns filled with animal charcoal (the capital cost of which "char" in a modern sugar-house is a very heavy item), might carry out treatment in a comparatively cheap and rapid manner with the use of a few tanks and filter-presses, and might also probably obviate the use of the Taylor filtering installation. Likewise, the manufacturer on the plantation making a white sugar suitable for direct consumption might so improve the appearance of his product as to make it equal, or almost so, to the home refined sugar. Lastly, the jam, confectionery, or biscuit manufacturer is offered a ready means of refining raw sugar sufficiently for his purpose.

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[28] *Intern. Sugar J.*, 1917, 247.

Although experiments have shown decolorising carbons undoubtedly to possess a remarkable power of adsorbing colouring matters, gummy substances, and to some extent also mineral matter from solutions of raw sugars, it must be admitted that efforts to realise these advantages economically in practice have not yet been successful.[31] Evidence is still lacking that any decolorising carbon on the market is capable of competing in the refinery with animal charcoal, which can repeatedly be revivified. Regarding the question of refining sugar on the plantation, H. C. Prinsen Geerligs[32] mentions that the experiments recently made in Java with "the new patented carbon 'Norit' appear not to have had the desired result, as the factory in which extensive experiments have been made still continues to sell refining crystals." At the present time the considerable expense of the decolorising carbon itself appears to be the chief obstacle in the way of this promising development, and the appearance on the market of a comparatively cheap and powerful preparation, capable of repeated revivification by boiling with alkali, or by other suitable means, would doubtless meet with a ready demand in the sugar industry. It is true that several disadvantages have been experienced in operating with these carbons, such as the difficulty in obtaining a clear filtrate, owing to the readiness with which the extremely fine particles pass through the filter-cloth, but none of these appears unsurmountable. Already, for example, it has been pointed out that dimness of the filtrate may be obviated by the use of a little kieselguhr to form a " pre-coat " over the surface of the fabric used in the presses.[33]

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[29] *Intern. Sugar J.*, 1911, 34, 496.
[30] *Ibid.*, 1914, 566; 1915, 70, 129; 1916, 517; 1917, 506.
[31] *Intern. Sugar J.*, 1918, 424.
[32] *Ibid.*, 1918, 64.

In view of the possible great future of decolorising carbon in the sugar industry, it is not surprising that much work has recently been carried out on its manufacture. Wood carbonised without previous treatment yields a carbon useless for decolorising purposes; but when three parts of sawdust are mixed with two of lime, and heated to 600°–1000° C., the resulting carbon has a decolorising power equal to that possessed by " Norit," as was found by the Committee of the Royal Society appointed to investigate the subject,[34] and also by M. A. Schneller[35] of the Louisiana Experiment Station. Such a process, however, is a comparatively costly one, since the charred mixture contains about 75% of calcium oxide and carbonate, which must be removed by solution in hydrochloric acid, about 6 tons of which is required to yield one ton of the finished product. When, on the other hand, a soluble salt, as potassium or sodium carbonate, which can subsequently be eliminated simply by washing with water, is used in the mixture to be carbonised, the result, as Schneller found (*loc. cit.*), is a carbon having an efficiency only 70% that of the Dutch preparation. More promising are the results obtained with the process of A. Zelniczek,[36] in which 1 part of sawdust and 2 of zinc chloride in solution are dried, heated in a retort to the volatilising point of the salt, and finally washed with water, a carbon having a decolorising power five times that of " Norit " being thus produced at a small cost for raw material, since the zinc chloride can almost entirely be recovered for repeated use. Similarly satisfactory results are stated to have been obtained by F. W. Zerban,[37] using tin chloride, and even better using anhydrous magnesium chloride. Some interesting experiments in the direction of producing a powerful and cheap preparation have been made at the Louisiana Experiment Station by W. G. Taggart[38] by carbonising rice hulls, rice straw, or rice chaff, and treating with sodium hydroxide to remove the silica, the resulting product (the patent rights for which have been claimed by H. M. Shilstone[39]) having a decolorising power about 1½ times that of " Norit." Lastly, it may be mentioned that F. W. Zerban and E. C. Freeland[40] have recently proposed to utilise kelp for the purpose, having found that by carbonising it rapidly in such a way that the gases can escape freely, and by later heating in a closed retort to redness for two hours and washing with water and a little acid, a product more powerful than "Norit" can be obtained.

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[33] *Intern. Sugar J*, 1918, 425.

[34] *Chem. Trade J.*, 1917, Sept. 15, p. 218; *J.*, 1917, 1041.

[35] *La. Planter*, 1917, 64, 154; *Intern. Sugar J.*, 1918, 191; *J.*, 1918, 316A.

[36] Austrian Pat. 68169; Fr. Pat. 471295; *J.*, 1915, 216.

[37] *La. Bulletin*, 161; *J.*, 1918, 480A.

[38] *La. Planter*, 1917, 63, 381.

[39] Eng. Pat. 116253; *J.*, 1918, 599A.

[40] *J. Ind. Eng. Chem.*, 1918, 10, 812; *J.*, 1918, 778A.

Defective sugars for refining.—R. S. Norris, during an investigation of the nature of the complaints made against the quality of the Hawaiian raw sugars in refineries in the United States, found that, compared with Cuban sugars, those from the Territory gave difficulty in the preliminary process of washing in the centrifugals, this operation being slower and requiring more water; they required a larger number of bags for filtration after defecation, and often gave a cloudy liquor; they caused the deposition of a heavy scale on the heating surfaces of evaporators and pans; and, lastly, in the production of "barrel syrups" (which are made from refinery final molasses by passing over char, and concentrating to about 80° Brix) there was cloudiness and sediment. The first defect was due to the small and irregular grain of the Hawaiian sugar, which Norris[41] points out should not contain more than 5% of crystals less than 0·75 mm. in diameter, and should be 1 mm. or more, but as regular in size as possible, though it may also be due in some degree to the high viscosity of the molasses adhering to the crystal. The second, third, and fourth defects may be traced to the presence in the sugars of this origin of a comparatively large amount of calcium sulphate, due probably to the practice in vogue in Hawaii of starting graining on low-grade products,[42] which grain is subsequently used as "seed" for the commercial sugar. G. Giacometti[43] mentions that already improvements have been effected in the direction of boiling to a larger and more regular grain, and that experiments with the object of eliminating the lime salts by suitable chemical treatment and filtration are in progress.

Valuation of raw sugars for refining.—Efforts have been made during recent years to elaborate a rough method of standardising raw sugars destined for refining, based on the size and hardness of the grain, the amount of insoluble matter, the reaction, and the odour, in addition to the usual data, such as the polarisation and the ash. But admirable as such methods are, they still fall short of what is desired, inasmuch as they are based on assumptions frequently not borne out in practice, and overlook important variations in quality radically affecting the value of the product for refining purposes.

W. D. Horne[44] attacks this question, presumably on account of the defective nature of raw sugars, just discussed, and he does so in a direct manner by examining the behaviour of the sugar when subjected to certain tests that imitate as closely as possible the conditions actually obtaining in the refinery. Thus, firstly, in order to obtain an indication of its "affinability," or the completeness with which the adhering film of molasses can be removed from the crystal, 200 grms. of the sample is mixed into a magma with 92 c.c. of a wash-liquor composed of a saturated solution of the sample itself, made by shaking 100 grms. with 45 c.c. of water for ten minutes and decanting, this magma being spun in a 5-in. laboratory centrifuge for two minutes and the yield of washed sugar and its polarisation determined. Under these conditions, a good centrifugal raw sugar, which during manufacture has not been mixed with "seconds," will polarise about 99·4°, and an ordinary centrifugal sugar about 99·0°; so, depending upon the purity of the washings below 80°, a deduction from the basic price of the raw sugar may be calculated. Secondly, the behaviour of the raw sugar during defecation and filtration is examined by treating a 45% liquor made from the sample with the minimum amount of acid calcium phosphate and calcium sucrate to produce a pure solution, heating to 190° F., and filtering through a cloth folded into a 3-in. perforated brass cone, the amount of phosphate employed and the time taken to collect 70 c.c. of the filtrate being noted. Sugars which filter freely in the refinery will require five minutes or less in this test, those of medium quality from 5 to 10 min., poor samples 10–15 min., and bad "gummy" samples 15–20 min., or even longer, and depending upon this rate of filtration the deduction to be made may be assessed. Thirdly, the readiness with which a raw sugar may be decolorised by animal charcoal is found by dissolving 10 grms. in 30 c.c. of water, adding 0·25 grm. of kieselguhr and 2·0 grms. of good animal charcoal in powder (which all passes through a 60-mesh sieve), raising gently to boiling-point, and filtering through paper, colorimetric tests of the filtrate and of a solution submitted to similar treatment in the absence of the animal charcoal affording the means of comparison. A sugar of average quality in this test will lose about 75% of its colour, and according to the greater amount of char work required than in a standard sample, the deduction to be made from the basic price may be ascertained. There are of course other factors that might be taken into account, such as the amount of ash present in the raw sugar, but the amount of salts present capable of preventing the crystallisation of sucrose from solution during graining (the so-called "molassigenic ash") is of less importance than the time and labour expended in carrying out the three refining operations here considered.

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[41] *Sugar*, 1918, **20**, 6.

[42] *Intern. Sugar J.*, 1918, 182; *J.*, 1918, 316A.

[43] *Ibid.*

[44] *J. Ind. Eng. Chem.*, 1918, **10**, 809; *J.*, 1918, 777A.

ANALYSIS OF SUGAR PRODUCTS AND METHODS OF CHEMICAL CONTROL.

Determination of sucrose.—During the past few years, several authorities, in particular the late H. Pellet, have contended that in order to realise the most precise estimate of the sugar losses during manufacture, direct polarisation is an insufficiently exact means of determining the sucrose content of the several products, and that the Clerget process of double polarisation must be applied throughout, not only in the case of juices and syrups, but even with raw sugars when these are of low purity. L. Fauque,[45] who now practises this system of uniform analysis, draws attention to the appreciable error that may be introduced by assuming the general validity of the divisor 144·0 used in calculating the percentage of sucrose when operating according to the original Clerget process. He has found that this figure is generally appreciably lower, varying between 141·6 and 142·6, depending upon the graduation of the saccharimeter used, and he points out that the divisor must be verified for each instrument and also for the system of calibration of flasks and pipettes in use. Neglect of this precaution when examining juices may cause the indication of too low a quantity of sugar entering the factory, and thus denote losses higher than might actually occur.

In the case of such an impure product as molasses, direct polarisation gives results far from the truth, and double polarisation is usually applied, though some few factories may employ a gravimetric or volumetric process depending upon the determination of the reducing sugars before and after inversion. Until a few years ago, the Herzfeld modification of the Clerget double polarisation process was almost always used, but V. Stanek[46] working with beet molasses, and later the writer of this report with the cane product,[47] showed that appreciable errors are introduced when this method is employed, for the reason that the difference between the readings before and after inversion is not due wholly to hydrolysed sucrose but also to the presence of certain optically active impurities, the rotation of which varies according to the reaction of the liquid. Thus, the direct reading taken in the presence of the basic lead acetate used for clarification is not comparable with that of the inverted liquid containing the hydrochloric acid used for effecting hydrolysis, and in order to obviate this both liquids must have the same degree of acidity, or must both be neutral.

Although exact results are obtainable by the use of invertase as the hydrolyst, as was shown by the writer of this report,[48] who used a modification of a method previously proposed by A. R. Ling,[49] the procedure is too lengthy for routine work, and in consequence a number of investigators have elaborated methods, which have been subjected to a careful comparative examination by T. van der Linden.[50] He found Pellet's process,[51] in which both readings are taken in the presence of approximately the same concentration of sulphurous acid, to give an excellently clarified liquid, while the results were equal to, or only slightly lower than, those given by Steuerwald's method[52] of effecting hydrolysis at the prevailing laboratory temperature (instead of 68°–70° C.), and also by that of Tervooren,[53] which until recently was official in Java factories. Deerr's method[54] was considered to be theoretically exact, and of value in special investigations, although too involved for routine practice; for which last reason E. Saillard's[55] was not examined. It was concluded that the several methods examined are all more complicated than Steuerwald's "cold inversion process," now adopted in Java, and that none can be recommended in preference to it, though a combination with it of Pellet's sulphurous acid procedure might advantageously be employed, as in this way the difficulty of reading dark-coloured liquids is overcome. It will be noted, however, that van der Linden's investigations, useful as they are, relate only to the comparison of different recently published processes one with another and not with any method known to give exact results. A valuable sequel to them, therefore, would be to determine to what extent the results given by the "cold inversion" process and Pellet's sulphurous acid process are comparable with those given by the invertase method, acknowledged to be capable of yielding results of absolute accuracy.

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[45] *Intern. Sugar J.*, 1918, 477; *J.*, 1918, 710A.

[46] *Zeitsch. Zuckerind. Böhm.*, 1906, 31, 417.

[47] *J.*, 1911, 62.

[48] *Intern. Sugar J.*, 1912, 89; *J.*, 1912, 244.

On the other hand, H. S. Walker[56] believes that the sulphurous acid process introduces the danger of inversion at the temperature prevailing in tropical laboratories, and advises the removal of the basic lead acetate used for clarification by the addition of an excess of phosphoric acid. According to his procedure, the normal weight solution of the molasses under examination is clarified by means of dry basic lead acetate (Horne's defecating reagent), filtered, treated with an excess of phosphoric acid, again filtered, and the direct reading taken. He claims that this method of clarification yields a pale yellow liquid, which can easily be read in the 400 mm. tube; and that, while the effect of the excess of the phosphoric acid upon the rotation of the invert sugar is not so pronounced as that of the 5 c.c. of hydrochloric acid used for inversion, the difference is so slight as to be negligible, the error due to the volume of the lead precipitate being at the same time obviated by the use of the dry basic lead acetate. Tests carried out with "reconstructed molasses" containing the impurities present in the factory product, and a known amount of sucrose, are said to have shown this modification to give results very closely approximating to the truth.

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[49] *J.*, 1898, 111.

[50] *Archief Suikerind. Ned.-Indië*, 1917, 25, 1249; *Intern. Sugar J.*, 1918, 139; *J.*, 1918, 161A.

[51] *J.*, 1897, 474.

[52] *J.*, 1913, 1025.

[53] *Archief Suikerind. Ned.-Indië*, 1904, 321.

[54] *Intern. Sugar J.*, 1915, 179; *J.*, 1915, 503.

[55] *Circ. Hebd. No* 1260–1262; *J.*, 1913, 836.

[56] *Intern. Sugar J.*, 1918, 239; *J.*, 1918, 385A.

Determination of reducing sugars.—Previous to carrying out the determination of "glucose" according to a gravimetric or volumetric method, it is generally considered necessary when examining cane molasses to clarify the solution with normal lead acetate in order to remove non-sugar substances that may possess a copper-reducing effect, and the question of a suitable reagent for removing the excess of lead remaining previous to boiling the liquid with Fehling's solution has been examined. Meade and Harris[57] had found that sodium carbonate, sodium sulphate, neutral potassium oxalate, and oxalic acid were each unsatisfactory, the first two because they appear to carry down some of the reducing sugars from solution, and the last two because the excess of the reagent remaining affects in some degree the reduction of the Fehling's solution. Disodium phosphate proved to be the most suitable, as it entirely removes the lead from solution, and an excess exercises no influence upon the reduction. R. S. Morris and A. Brodie[58] have now confirmed this result, and recommend that this method of "de-leading" should be specified in the official methods of chemical control adopted in the factories of Hawaii, replacing neutral potassium oxalate hitherto prescribed.

Determination of dry substance.—The desiccation method of determining dry substance (or conversely the water content) of sugar factory products has long given rise to criticism, and the unsatisfactory results it may give in the case of cane molasses are illustrated in some figures supplied by L. G. L. Steuerwald.[59] Collating the results obtained by European and native assistants in factories in Java, where the Josse method of drying to constant weight on a coil of bibulous paper is followed, he found values varying between as much as 76 and 84%, and concluded that this procedure as now prescribed is unsuitable for routine factory work. An effort to evolve a better method, in respect of rapidity as well as accuracy, has been made by T. van der Linden,

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[57] *J. Ind. Eng. Chem.*, 1916, 8, 504; *J.*, 1916, 750.

[58] *Intern. Sugar J.*, 1918, 238; *J.*, 1918, 386A.

[59] *Archief Suikerind. Ned.-Indië*, 1917, 25, 1417; *J.*, 1918, 161A.

M. Kauffman, and F. Leistra[60] by distilling the product with a volatile and immiscible liquid, *e.g.* xylol, and measuring the water carried over in a suitably calibrated cylinder; a similar process, it will be remembered, was applied some years ago by Urich for the determination of water in bagasse.[61] By regulating the time of distillation, and applying a "meniscus correction" or allowance for the water absorbed by the immiscible liquid and that lost by volatilisation, results can be obtained agreeing well with those indicated by the refractometer. Although purely an empirical one, this method may prove useful in careful hands for the rapid routine examination of molasses and other products of a similar class.

Determination of ash.—According to results obtained by A. Schweizer,[62] it may happen in determining the ash of sugar products by the usual process of sulphating, that during the incineration a part of the sulphates may be reduced to sulphides, which error may of course be corrected by further treatment with a few drops of sulphuric acid. Thus, he found when examining Java cane molasses that the sulphated ash as ordinarily determined was 9·52%, and that on re-treating with sulphuric acid (when sulphuretted hydrogen was evolved) the figure became 10·56%, agreeing with the result obtained by sulphating the carbonated ash—namely, 10·46%. In the same paper, Schweizer observed that he had found the customary deduction of 10% for converting the sulphated or so-called "true ash" to be far from correct in the case of Java molasses, a remark that was corroborated by the writer of this report and J. H. Lindfield,[63] who gave the results of determinations made with a number of cane and beet sugars and molasses from different countries. Even in products of the same class considerable differences were found. Thus, in the case of beet sugars it varied from 12 to 25%, but was never as low as 10%; in that of beet molasses from 12 to 18%; and in that of cane molasses from 14 to 21%; but with cane sugars the values were very irregular, fluctuating between 6 and 26%. Varying factors, it was pointed out, are to be expected with cane sugars, owing to the presence in them of greater or less amounts of insoluble matter, which is partly sand, and partly salts thrown out of solution during evaporation and boiling and retained during curing in the centrifugals. In determining the ash of sugars destined for the refinery, therefore, a filtered solution should be used, since it is the soluble ash that is of importance for the assessment of the possible yield of the sample, and these writers suggest that this condition should be recognised generally in the commercial analysis of raw sugars.

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[60] *Archief Suikerind. Ned.-Indië*, 1917, **25**, 951; *Intern. Sugar J.*, 1918, 89; *J.*, 1918, 218A.

[61] *Intern. Sugar J.*, 1913, 80.

[62] *Ibid.*, 1918, 138.

[63] *Ibid.*, 1918, 114; *J.*, 1918, 254A.

Miscellaneous.—Some experiments published on the preservation of sorghum juices by D. O. Spriesterbach[64] should prove of interest to the sugar factory chemist as a means of preventing the decomposition of periodic composite samples. He found that by neutralising the juice with a slight excess of calcium carbonate, boiling, adding 2 grms. per litre of sodium carbonate, and afterwards potassium mercuri-iodide to the amount of 0·05 to 0·10%, no loss of sucrose occurred during several months, while good results were also obtained without boiling by saturating the juice with toluene after the addition of the potassium mercuri-iodide preservative.

In order to facilitate the calculation involved in determining the purity of mill juices and other liquors from the density and the polarisation, A. F. Blake[65] recommends the so-called "nomographic reckoner" devised by H. G. Deming,[66] which enables one almost instantly to obtain results to four figures with an error of one unit only in the last place; and this device might also be applied with advantage, nod oubt, to other somewhat complicated routine computations in the sugar factory, such as those concerning the percentage evaporation, the proportions of syrup and molasses to be boiled, or the possible available yield.

In a paper on the reading of sugar solutions in the polariscope, H. Pellet[67] claimed to have noticed that, if after a first observation the tube containing the liquid be rotated 90° upon its axis, a second reading may differ from the first by several tenths of a degree, for which reason he advocated the use of a tube similar to that used for Clerget inversion observations; upon one of the caps of this tube a mark is made indicating the end which must always be set towards the observer, thus ensuring that the tube shall always be in exactly the same position in the trough of the instrument. These recommendations are worthy of note, though with well-made tubes and selected cover-glasses, and the observation of the usual precautions, such anomalous readings should not be obtained.

In molasses distilleries, after fermentation has ceased, there remains a greater or less amount of unfermentable reducirg sugars, to which the collective name of glutose has been given, and for the determination of these C. Muller[68] has satisfactorily followed Pellet's procedure[69] of clarifying with lead acetate, removing the excess of lead from solution, and ascertaining the cupric-reducing power of the filtrate by heating for thirty minutes at the reduced temperature of 65° C. Operating in this way, he found the amount of unfermentable sugars to lie between 3·2 and 4·9% for cane molasses, and 0·1 and 0·2% for the beet product, the quantity in the former case for the same factory being found to vary somewhat according to the ripeness of the cane crushed.

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[64] *J. Amer. Chem. Soc.*, 1918, **40**, 431; *J.*, 1918, 217A.

[65] *Intern. Sugar J.*, 1918, 73; *J.*, 1918, 217A.

[66] *J. Amer. Chem. Soc.*, 1917, **39**, 213.

[67] *Intern. Sugar J.*, 1918, 88.

[68] *Archief Suikerind. Ned.-Indië*, 1918, **26**, 346; *Intern. Sugar J.*, 1918, 377; *J.*, 1918, 556A.

Chemical control of the factory.—In Java the new system of chemical control published a short time ago[70] has now been instituted in the factories of that progressive sugar-producing colony; and, though it is open to criticism on the ground of its rather involved and intricate nature, its value has unquestionably been demonstrated. Hitherto it has been customary to consider the sucrose present in the cane to be the sum of that in the extracted juice and that remaining in the residual bagasse, thus making no allowance for losses that may occur, and have been suspected to occur, during the process of milling. But according to the new procedure, the sucrose content and the volume of the juice from each of the units of the multiple milling plant are assessed separately, the figure found being compared with that for the total mixed juice. H. C. Prinsen Geerligs[71] states that in some factories a loss of sucrose as high as 6% of the total quantity can be detected in this way, these losses being the result simply of the fermentation of the juice aided by the favourable temperature prevailing. It is seen, therefore, that continuous disinfection during milling becomes a matter of urgent necessity, and in order to reduce the considerable losses that may occur in this way it has not been thought too much trouble or expense by some superintendents to instal a duplicate set of tanks, gutters, collectors, stone-catchers, &c., so that while one is in operation, the other may be cleaned.

Interesting figures have been collated by Prinsen Geerligs[72] for Java, where all the factories take part in a uniform and very thorough method of chemical control. During the year under review, 1917, the sucrose content of the cane was the highest yet observed, namely 12·82% while the fibre content, which until 1916 had gradually increased, now appears to have reached a maximum at 13·02%. The sucrose extracted by the mills was 92·3%, another record figure so far as this country is concerned, though it is still lower than the figure now general in Hawaii and in Cuba. The sucrose lost in the filter-press scum has reached the satisfactory figure of 0·80% of the sucrose in the juice, or 0·09% on the cane, this lower value being presumably a consequence of the increased manufacture of plantation white sugar, in the preparation of which a harder and more readily exhausted cake is obtained. Notwithstanding the influence of the heavier crushing by the mills, which tends to raise the content of non-sugar substances, the quotient of purity of the raw juice has likewise been higher during 1917 than in any previous season, amounting to an average of 85·8° with extremes of 91·4° and 80·2°. Prinsen Geerligs a few years ago elaborated a method of calculating the maximum available yield of sucrose from the juice, according to which [73] the only losses taken into account are those in the filter-press cakes and the molasses, the unaccountable losses not being considered. On applying this formula during the 1917 crop, it is interesting to notice that a figure of 11·40% of the cane was indicated. As the sucrose extracted was 11·0%, there is a difference of 0·40%, a figure which agrees very well with the unaccountable losses assessed directly—namely, 0·36% of the cane.

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[69] *Intern. Sugar J.*, 1917, 275.

[70] "Handleiding ten deinste der Molencontrôle," Bulletin No. 2, issued by the Proefstation voor de Java-suikerindustrie, technische afdeeling, Pekalongan, Java, 1917.

[71] *Intern. Sugar J.*, 1918, 63.

[72] *Ibid.*, 1918, 460.

SUGAR MANUFACTURE FROM PALM, SORGHUM, AND MAPLE.

Palm.—At the present day about 500,000 tons of sugar is produced annually from palms, mostly in India for consumption by the natives. In a paper discussing the relative merits of the palm and cane as commercial sources of sugar, H. E. Annett [74] points out that the advantages offered by the former are the certainty of yield year after year, the small cost of upkeep of the plantation, the production in the form of juice, no crushing machinery as in the case of cane being required, and the simple clarification treatment necessary. On the other hand, disadvantages are the lack of fuel corresponding to the bagasse of the cane sugar industry, the long period (about six years) until the trees can be tapped for sap, the difficulty of collecting the juice, and lastly the low content of sugar in the juice. However, since it is probable that much higher yields of sugar per acre could be obtained from palms, particularly the *Nipa fruticans* variety, than from sugar cane, it is considered that the advantages seem to outweigh the disadvantages. In a small factory in the Jessore district in India some high quality white sugars, which found a ready sale locally, were produced from palm juice without any special treatment being required during manufacture, concentration being effected in vacuum pans.

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[73] *Intern. Sugar J.*, 1912, 274; *J.*, 1912, 550.

[74] *Intern. Sugar J.*, 1918, 324.

Sorghum.—With the object of finding a readily cultivated source of sugar, sorghum was planted experimentally in 1917 in different parts of France by D. Berthelot and R. Trannoy,[75] and it was found to grow well everywhere. Seed was planted on April 25, and periodic analyses of the juice showed that the maximum richness was reached in October, when the sucrose and reducing sugar contents were 14·04 and 1·03 grms. per 100 c.c. respectively. During the next six weeks the sucrose content remained between 12 and 14%, but following this it decreased rather rapidly, the reducing sugars at the same time increasing. But as other writers have pointed out, it was found that although sorghum can be cultivated cheaply, it produces a juice from which sucrose cannot easily be crystallised. Moreover, it is very susceptible to frosts.

Maple.—A very exhaustive account of the maple sugar industry as carried on in the United States has been published by A. H. Bryan and collaborators.[76] A single tree yields 12–24 galls. of sap during a season, lasting for about three weeks during the year, and 1 lb. of sugar is obtained from 4½–6 galls. Various products are made from the sap, as syrup, and different forms of sugar. Regarding the chemical standards with which genuine maple syrup should comply, the results of a study of 481 samples examined in 1910–12 gave the following average figures, to which may also be added those for the Canadian product published by A. McGill,[77] established on the basis of the examination of 456 samples in 1914.

	United States samples.	Canadian samples.
Total ash per cent.	0·77	0·60
Insoluble ash per cent.	0·23	0·12
Lead number (Winton)	1·85	1·20
Lead number (Canadian)	2·60	1·70
Malic acid value	0·60	..

STARCHES AND GUMS.

Several processes for the preparation of vegetable glue have been protected. After digesting starch paste with sodium hydroxide in the known manner, R. W. Tunnell [78] adds alum or aluminium sulphate in quantity depending upon the degree of viscosity required; while the same inventor,[79] in order to render the glue waterproof, mixes zinc chloride with the paste treated with alkali as usual. C. R. Robinson [80] describes a procedure in which dry starch is treated with sodium bisulphate and sodium hydroxide, and mixed with trisodium phosphate and water with or without ammonia, the mixture being subsequently heated and neutralised, and treated with cuprammonium sulphate, with or without the addition of casein. Since vegetable glues containing free alkali are liable to injure surfaces with which they come into contact, V. G. Bloede [81] neutralises by the injection of sulphur dioxide or carbon dioxide. A preparation for sizing yarn, which will not only penetrate the cloth, giving it body and weight, but will also coat the fibres, strengthening them, is made by A. W. H. Lenders [82] by modifying starch with acid under conditions which produce a thin boiling starch, and adding raw starch, the whole being subsequently treated with alkali. Finally, in order to produce a gum suitable for stiffening and sizing, W. Alexander [83] adds borax to a solution of gum arabic, and evaporates the liquid to dryness, or alternatively mixes together powdered gum arabic and powdered borax.

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[75] *Comptes rend.*, 1916, **166**, 824.

[76] *U.S. Dept. Agric.*, Bull. 466 of 1917; *J.*, 1918, 277A.

[77] *Lab. Inland Rev. Dept., Ottawa*, Bull. 409 of 1918.

[78] U.S. Pat. 1248039; *J.*, 1918, 67A.

[79] U.S. Pat. 1266354; *J.*, 1918, 523A.

[80] U.S. Pat. 1267699; *J.*, 1918, 599A.

[81] U.S. Pat. 1269678; *J.*, 1918, 599A.

[82] U.S. Pat. 1253397; *J.*, 1918, 189A.

[83] U.S. Pats. 1263634 and 1263635, *J.*, 1918, 386A.

ELECTRO-CHEMISTRY.

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During the past year progress in electro-chemistry has been well maintained. Much of the work has been accomplished in America, but in Great Britain solid advance has been made in spite of the fact that almost all our energies have been directed to the prosecution of the war to a successful issue. The outstanding developments may be briefly indicated. The perfecting of film rectifiers and condensers has occupied much attention, as well as the general subject of electrolytic deposition, which is now applied to the moulding of vessels according to pattern, such as crucibles, &c. A new process for the measurement of conductivity in electrolytes has been devised, which marks an important departure from the time-honoured method of Kohlrausch. The Cottrell process of dust and mist deposition, as applied to the purification of gases, has been widely employed in chemical industry, and various improvements introduced in connection with it. The refining of metals has not been much to the front, but on the other hand extra attention has been given to the electrolytic extraction of metals, particularly zinc, copper, nickel, and magnesium.

A curious development in the electrolysis of water is the invention of cells for producing electrolytic gas for use in internal combustion engines; several cells for the separate collection of hydrogen and oxygen have been recorded.

Chlorine and caustic soda have occupied considerable attention, and the importance of the chlorine aspect of this industry has been emphasised.

The production of per-salts by electrolysis is making good progress, and the separation of the rare earth hydroxides by electrolytic precipitation has received further consideration. A departure in this sphere is the production of alkali metal salts by the electrolytic treatment of insoluble natural silicates.

In the province of organic chemistry, the only development of importance is the breaking down of hydrocarbons of high molecular weight in the presence of methane or natural gas by the action of the electric discharge. Mineral oils of low boiling-point can be synthesised by this means.

By far the largest volume of work published has related to developing and modifying the electric furnace. Electro-metallurgists in this country have made very important contributions to this development. Half the electro-chemical literature of the year, if not more, deals with the electric furnace and products thereof. Nearly all this work relates to the arc furnace and the resistance furnace.

In electro-analysis some advance is recorded, the outstanding feature of which is the development of the electrometric method of titration, which has been particularly applied to the estimation of certain metals in special steels.

ELECTRICAL POWER.

The importance of cheap electrical power to the industries of the country is now realised in Government circles, and the establishment of large power centres is to form an item in the "reconstruction" programme. Much might be done for electro-chemical industries by utilising to the full the surplus power of collieries and blast-furnaces, where generating plant is seldom worked to its full capacity. The load factor in these industries is seldom above 50%, and it is held in many quarters that by utilising power of this description its cost will become equal to, if not less, than the cheapest water power. At least one carbide maker[1] has succeeded in surmounting the difficulties entailed in working with intermittent electric power of this class.

PRIMARY AND SECONDARY BATTERIES. DEPOLARISERS.

Methods for restoring exhausted Leclanché cells continue to be devised, and several fresh voltaic cells have been described in which zinc is generally employed as the negative element, combined with a carbon positive immersed in some suitable depolarising fluid. The Lelande cell has been developed to some extent, and in one case the copper oxide plate has incorporated with it an oil which holds sulphur in solution and has the effect of increasing the voltage of the cell.[2]

The Lelande idea is utilised in another type[3] by replacing copper oxide by oxyarsenide or oxyphosphide of iron; polarisation by discharged hydrogen is prevented by the formation of phosphoretted or arseniuretted hydrogen, which passes off freely from the plate.

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[1] C. Bingham, *J.*, 1918, 85 R.

[2] R. C. Benner and others, U.S. Pat. 1255283; *J.*, 1918, 213A.

[3] M. R. Conrad and others, U.S. Pats. 1262019, 1262020; *J.*, 1918, 339A.

In another single-fluid cell[4] with zinc and carbon plates, the electrolyte is a solution of ferric salt, which acts as a solvent on the zinc plate and as a depolariser on the carbon. Local action, it is claimed, is small, and the exhausted electrolyte can be regenerated by chlorination. The reaction supplying the chemical energy is

$$Zn + 2FeCl_3 = ZnCl_2 + 2FeCl_2.$$

Acidified potassium permanganate has been advocated as an efficient depolariser of the carbon plate, which may be contained in a porous vessel; zinc is the negative plate in a strong solution of the sulphate of that metal and a solution of caustic alkali. In the last-named case a constant electromotive force of 2·7 volts is claimed.[5] An attempt to convert the energy liberated by the oxidation of carbon directly into electrical energy has produced another carbon cell,[6] in which the electrolyte consists of fused borax containing manganese dioxide. The negative carbon floats on the fused mass, and the positive plate consists of strips of gold foil at which the fused electrolyte is oxidised; the electrolyte is deoxidised by the carbon plate with the production of carbon monoxide and dioxide; the E.M.F. at 935° to 990° C. is approximately 0·8 volt. The construction is not that of a true carbon-oxygen cell, but is really an electro-chemical oxidation and reduction combination.

The depolarising action of manganese dioxide[7] in cells of the Leclanché type is the subject of many patents this year. The activity of the substance is improved by preparing it according to special instructions, which include the precipitation of the hydrated peroxide from manganese chloride or sulphate solution by special reagents, and the decomposition of alkali manganate or manganite with steam. Two new depolarisers for electric batteries are copper oxide[8] which has been reduced and subsequently oxidised in the presence of sulphur, and molybdenum trioxide,[9] which is put forward as an efficient substitute for manganese dioxide.

It has already been shown that sulphurous acid can be converted to sulphuric acid by anodic oxidation and a good yield of the latter acid obtained, and in continuation of this work, sulphurous acid is suggested as a suitable and efficient anodic depolariser[10] for industrial work, presumably for the extraction of such metals as copper, nickel, and zinc, by the electrolysis of solutions obtained by leaching roasted ores with sulphuric acid. The lowering of the anode potential at platinum electrodes was found to amount to as much as 1·5 volt, provided current density did not exceed 6 to 10 ampères per square decimetre.

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[4] E. Sokal, U.S. Pat. 1258266; *J.*, 1918, 273A.

[5] R. Schuster, Eng. Pat. 114012; *J.*, 1918, 249A.

[6] S. A. Read, Amer. Electrochem. Soc., May 1918; *J.*, 1918, 311A.

[7] C. Ellis, U.S. Pats. 1269913, 1269914; J., 1918, 593A. M. E. Holmes U.S. Pat. 1259099; *J.*, 1918, 311A.

[8] H. F. French, U.S. Pat. 1269173; *J.*, 1918, 592A.

[9] M. E. Holmes, U.S. Pat. 1272952; *J.*, 1918, 593A.

Secondary plates have received much attention during the past year, mainly with a view to increase the surface efficiency, prevent disintegration, and diminish the weight of the batteries. The lead supporting plates are either made according to special design and subsequently packed with the usual lead oxide mixture,[11] or they may be packed with a special mixture of amorphous and crystalline litharge to ensure decrease in weight combined with great porosity.[12] According to another patent the supporting grid is constructed of a phenolic condensation product, and the active material is packed into the pores of the framework.[13] The capacity of the Edison battery may be increased by the addition of lithium hydroxide to the alkaline solution generally employed.[14]

ELECTROLYSIS. ELECTRODES.

The literature of the year does not reveal much development in the superimposing of alternating current on direct current for electrochemical work, though its usefulness in the case of gold refining and the electrolytic production of ozone has been proved. The production of metallic sulphides[15] by electrolysing a solution of thiosulphate between electrodes of the metal, the sulphide of which is required, is of interest.

Film-forming electrodes and electrolytes have received much attention in connection with the construction of lightning arresters, condensers, and rectifiers. Ammonium borate[16] acidified with boric acid is claimed as a good electrolyte for this class of cell. Citrate and tartrate solutions have been used largely, hitherto, for this purpose, and recently the addition of small amounts of alkali arsenites or arsenates[17] has been advocated to obviate the formation of fungus growths on the cell plates, which spoil the film-forming capacity.

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[10] M. de K. Thompson and A. P. Sullivan, *Met. and Chem. Eng.*, 1918, **18**, 178; *J.*, 1918, 213A.

[11] C. S. Palmer, U.S. Pat. 1251412; *J.*, 1918, 156A. I. Chkliar, Eng. Pat. 102976; *J.*, 1918, 96A.

[12] U.S. Light and Heat Corpn., Eng. Pat. 112133; *J.*, 1918, 96A.

[13] T. Spencer and others, U.S. Pat. 1260472; *J.*, 1918, 311A.

[14] L. C. Turnock, Amer. Electrochem. Soc., Oct. 1917; *J.*, 1917, 1279.

[15] H. B. Weiser, *J. Phys. Chem.*, 1918, **22**, 78; *J.*, 1918, 248A.

[16] L. W. Chubb, U.S. Pat. 1270784; *J.*, 1918, 593A.

A peculiarly designed cell[18] has been developed for this work, in which the metallic electrodes are insulated in an ingenious fashion so as to avoid the use of insulating pads or blocks, which are often responsible for the breakdown of the film. Aluminium is the metal generally employed, but magnesium and tantalum also give good results; the films possess high dielectric properties and offer strong opposition to the passage of current from electrode to electrolyte, but not to a current in the reverse direction.

Several fresh electrode potential determinations have been recorded recently, and a knowledge of these has considerable value for industrial processes, since this factor has an important influence on the course of the reaction proceeding at the electrode surface.

Copper-nickel alloys have been proved[19] to exhibit very regular electro-chemical behaviour in electrolytes containing the corresponding ions, and the potential values are reproducible and constant to within a few millivolts. On the other hand the same investigators have confirmed the fact that zinc-copper alloys are subject to unexplained changes, and they give potentials which are not generally reproducible. The divergent results obtained for chromium electrode potentials[20] are probably due to the fact that active and passive forms of the metal exist. Cast lead, electrolytic lead, and lead amalgam[21] give the same electrode potential values, but lead which has been immersed in a solution of the nitrate, containing nitric acid, gives a value several millivolts higher, which indicates that an allotrope of lead exists.

Two types of electrode suspension have been introduced, particularly applicable to copper refining; one[22] is for suspending the plates of crude copper used in the series system by lugs which rest on ledges projecting from the sides of the vat, so that they are totally submerged, and consequently there is no weakening or breaking of the plate at the electrolyte surface. The other[23] involves the use of aluminium connecters for the anode plates, by which they are suspended so that they are submerged, and the aluminium oxide formed by anodic action on the connecters renders them immune from corrosion by the electrolyte.

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[17] J. Coulson, U.S. Pat. 1255391; *J.*, 1918, 213A.

[18] L. W. Chubb, U.S. Pat. 1250141; *J.*, 1918, 156A.

[19] N. T. Gordon and D. P. Smith, *J. Phys. Chem.*, 1918, 22, 194; *J.*, 1918, 270A.

[20] A. W. Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 812; *J.*, 1918, 307A.

[21] F. H. Getman, *J. Amer. Chem. Soc.*, 1918, 40, 611; *J.*, 1918, 311A.

[22] H. H. Stout and others, U.S. Pat. 1267141; *J.*, 1918, 552A.

[23] J. H. Gilles and others, U.S. Pat. 1267653; *J.*, 1918, 553A.

ELECTRO-OSMOSIS. COLLOIDS.

Electro-osmotic processes have developed considerably during the last three or four years, and have been very largely applied to the desiccation of substances by electrolysis and the separation of crystalloids from colloids, as well as the separation of different colloids from each other. Recently the dehydration of the solid matter in an emulsion has been accelerated by driving it to a rotating anode surrounded by cathodes which press the deposited material.[24] Another modification,[25] applied to the dehydration of steatite, is the introduction of an electrolyte and a colloid in the emulsion, which it is claimed breaks up the material more finely and hence effects a more complete dehydration with the same expenditure of energy.

The manufacture of plumbago and clay crucibles by electro-osmosis is the subject of a recent patent. The suspended substance was at first driven to an absorbent mould placed between anode and cathode, on which the article of required shape was deposited. Subsequently, it was found that the absorbent mould may be dispensed with, and the clay or plumbago is electrolytically driven directly on to an iron mould which is also an electrode.[26] Increased potential results in increased pressure of material and denser formation of dry material.

The measurement of the rate of flow of solutions through diaphragms under electrical pressure has been continued, and an endosmometer has been devised for this purpose. The rate is apparently proportional to the potential applied and increases with rise of temperature; adsorption of ions by the diaphragm is suggested as the explanation of the phenomenon.[27]

The colloidal nature of soap solutions has been further studied by J. W. McBain[28] and his co-workers, who classify such as colloidal electrolytes probably containing highly charged aggregates or micelles which are highly hydrated but possess the mobility of an ordinary ion. The presence of such aggregates would account for the high conductivity of soap solutions, which is certainly not due to hydroxyl ions, since these workers have shown that the degree of hydrolysis of soap solution and hence the number of hydroxyl ions is quite small.

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[24] A. Gerlach, Ger. Pat. 305217; *J.*, 1918, 615A.

[25] Elektro-Osmose A.-G., U.S. Pat. 1266330; *J.*, 1918, 415A.

[26] B. J. Allen, Eng. Pats. 111762, 111775; *J.*, 1 18, 59A.

[27] T. R. Briggs and H. S. Bennett, *J. Phys. Chem.*, 1918, 22, 256; *J.*, 1918, 380A.

[28] *J.*, 1918, 249T.

Colloidal tungstic acid for curative purposes is made by striking an arc between tungsten electrodes, by which means the finely divided oxide is formed, and passing upwards, it becomes absorbed by a stream of distilled water.[29]

CONDUCTIVITY. RESISTANCE. INSULATORS.

A new method has been suggested by E. Newbery[30] for measuring the conductivity of solutions. The method is simple and depends upon the principle frequently used in measuring the resistance of a metal conductor by estimating the fall of potential between two points while a direct current of known strength is passing; it is claimed that all errors due to polarisation at the electrodes are eliminated. The method of Kohlrausch has been for so long the only one in use, and his values for potassium chloride solutions have been employed so extensively for standardising conductivity vessels, that it is refreshing to find a new and improved process available, and to see criticism levelled at the assumptions which are accepted in the Kohlrausch method.

Further work with resistance alloys[31] has shown that alloys of high resistance are made by mixing those metals which form solid solutions; such are nickel-manganese and nickel-chromium. Ternary alloys have a higher resistance than binary alloys of similar composition, and the greatest resistance is shown by iron-nickel-chromium and iron-nickel-manganese alloys.

The usual insulating mixtures[32] are still being evolved, in which pitch and a siliceous substance are the chief constituents, but the introduction of chlorinated hydrocarbons[33] in place of asbestos is increasingly advocated, and provides a flexible insulator which is also non-inflammable. It certainly seems that chlorine is to play an important part in future in the preparation of insulating materials.

Wood separators for accumulator plates are subjected to the treatment of various chemicals prior to use. Treatment with hypochlorite solutions[34] has been recently advocated, and the use of felt or asbestos[35] separators has been patented. Sparking plug insulators should be made of magnesia instead of porcelain, according to P. H. Brace,[36] since current leakage is appreciable with the latter substance. In the neighbourhood of 1000° C. it was found that porcelain acts as a storage battery when subjected to the action of an electric current, and it has a lower resistivity than magnesia, probably because it is a mixture of mutually soluble oxides.

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[29] W. S. Simpson, Eng. Pat. 113505; *J.*, 1918, 222A.

[30] *Chem. Soc. Trans.*, 1918, 113, 701; *J.*, 1918, 638A.

[31] M. A. Hunter and F. M. Sebast, *J. Amer. Inst. Metals*, 1917, 11, 115; *J.* 1918, 32A.

[32] A. R. Müller, Eng. Pat. 116532; *J.*, 1918, 474A.

[33] C. Ellis, U.S. Pats. 1246809 and 1248638; *J.*, 1918, 62A, 63A.

ELECTROSTATIC PRECIPITATION.

The Cottrell[37] process for precipitating solid particles from fluids (gases) has been widely utilised recently, particularly in sulphuric acid works, both for removing all dust from the sulphur dioxide mixture prior to its passage through the contact chamber, and also for removing sulphuric acid mist from the gases passing from the concentrating plant. Generally a uni-directional current of high voltage is used to charge a system of wires which are suspended axially in tubes or between plates, and as the gases to be treated pass through the treater the solid particles become charged and are carried with the discharge current to the receiving plate or tube. The process is evidently solving the dust problem, and has been used for recovering alkali salts from the dust of blast-furnaces and cement kilns.[38] In the tube and wire system it is proposed to enlarge the cross-section of the wires at those regions where they enter the tubes, in order to reduce the field intensity, which at these points tends to become excessive. The same object may be attained by covering a short length of each wire at these exposed regions with an insulating material.[39]

In order to keep the receiving electrode clean, a stream of liquid (water) may flow continually over its surface. This carries with it the deposited particles and prevents the formation of discharge points on the receiving plate itself.[40] A mechanical scraping arrangement can also be employed to keep the receiving electrode clean.[41]

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[34] H. Leitner, Eng. Pat. 117121; *J.*, 1918, 519A.

[35] J. Becker, U.S. Pat. 1256864; *J.*, 1918, 249A.

[36] Amer. Electrochem. Soc., April, 1918; *J.*, 1918, 417A.

[37] H. J. Bush, *J.*, 1918, 389R. A. A. Heimrod and H. D. Egbert, *Chem. and Met. Eng.*, 1918, **19**, 309; *J.*, 1918, 729A.

[38] L. Bradley, *Chem. and Met. Eng.*, 1918, **19**, 457; *J.*, 1918, 653A.

[39] W. A. Schmidt and others, U.S. Pat. 1252183; *J.*, 1918, 197A.

[40] H. A. Burns, U.S. Pat. 1250088; *J.*, 1918, 114A.

[41] C. W. Girvin and others, U.S. Pat. 1252104; *J.*, 1918, 142A.

The method is now applied to the removal of tar and other impurities from coal-gas,[42] and it has also been employed to accelerate the combination of nitrogen and hydrogen in the synthesis of ammonia, by causing the gas to combine with a substance (hydrogen chloride) to form a solid suspension, which is then removed by electrostatic means, and the clear mixture of hydrogen and nitrogen is then returned to the catalyst, where more ammonia is formed.[43] This process may also be utilised for accelerating the formation of ozone by causing it to combine with a hydrocarbon to form a solid ozonide, which may then be electrostatically precipitated.

For separating liquids from an emulsion[44] an electrical device has been patented in which use is made of the different resistances of the ingredients to operate an electro-responsive valve which releases the heavier liquid from the separator when sufficient has collected. The separation may also be facilitated by causing the stream of emulsion to pass between active electrodes.

REFINING OF METALS.

Progress in the literature of refining has been inconsiderable during the past year. In the case of copper, the adoption of a slanting position of the bipolar electrodes used in the series system has been patented. It is claimed that this prevents the slimes from being carried mechanically to the cathodes.[45]

For refining zinc, the idea has been advanced of enclosing the anode in a bag in order to keep the cadmium sludge in contact with the anode and thus prevent it from dissolving, as it will do if allowed to fall to the bottom of the vat and lose contact with the zinc in the anode.[46] The presence of iron in the bath up to a concentration of 1 grm. per litre has rather a beneficial effect.

Tin refining from a fluosilicate solution has received considerable attention. Free hydrofluosilicic acid is necessary, and the addition of various substances, including colloids, improves the deposit.[47] Possibly perchloric acid will be found useful for this work, since it has already been utilised for the electro-deposition of lead.

[42] *Gas J.*, Aug. 13, 1918; *J.*, 1918, 365R.

[43] W. A. Schmidt and others, U.S. Pat. 1252726; *J.*, 1918, 149A.

[44] C. W. McKibben, U.S. Pats. 1276386 and 1276387; *J.*, 1918, 678A.

[45] J. B. Herreshoff, U.S. Pat. 1262045; *J.*, 1918, 339A.

[46] Electrolytic Zinc Co., Eng. Pat. 108312; *J.*, 1918, 518A.

[47] E. F. Kern, *Chem. and Met. Eng.*, 1918, 18, 508. Amer. Elect. Soc., May 1918; *J.*, 1918, 424A.

EXTRACTION OF METALS.

The number of papers and patents which deal with the electrolytic extraction of metals has been very considerable, and it is evident that the difficulties and prejudices of earlier years are being slowly and surely overcome. Most of the investigations and advances relate to the extraction of copper, zinc, magnesium, and nickel, but iron and antimony have received some attention. The outstanding development of the past year is, undoubtedly, the rapid increase in the electrolytic production of magnesium and zinc.

The method of leaching oxidised copper ores[48] with dilute sulphuric acid for subsequent electrolysis is rapidly extending, and two new plants are reported from America.

Mixed lead-zinc ores are being increasingly treated by sulphatising roasting, followed by leaching with sulphuric acid, and electrolysis for obtaining the lead.

Electrolytic separation of copper and nickel has presented many difficulties, and novel means are being employed to render the process successful. In one case the nickel is first deposited by employing a sulphate solution as electrolyte, and an insoluble reagent such as calcium carbonate is packed around the nickel-copper anode in a porous cell, which has the effect of precipitating the copper as carbonate, whilst nickel sulphate goes into solution and the metal is deposited on the cathode.[49] In another process,[50] the copper is prevented from co-depositing by periodic reversal of the current (ten times per minute), which causes the copper deposited on the cathode during any interval to be driven back to the anode (temporary cathode), where it is deposited in such a loose state that it falls to the bottom of the vat.

A novel method for preventing polarisation[51] by gases during electro-deposition, particularly to be applied in the case of zinc and copper, is to work *in vacuo* or under reduced pressure. By this means, gas is not able to collect on the electrodes, and the process mitigates all gas troubles such as increase in resistance, precipitation of zinc oxide on cathode, and loose deposits, and is said to increase the rate of deposition of metal.

It has been demonstrated that the reduced efficiency observed when electrolysing copper sulphate containing iron sulphate, between lead electrodes, is due to reduction of ferric salt at the cathode and oxidation of ferrous salt at the anode.[52]

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[48] A. L. Walker, *Eng. and Min. J.*, 1918, 105, 94; *J.*, 1918, 152A.

[49] G. A. Guess, U.S. Pat. 1251511; *J.*, 1918, 155A.

[50] J. H. Gillis and others, U.S. Pat. 1260661; *J.*, 1918, 310A.

[51] A. A. Lockwood, Eng. Pat. 114976; *J.*, 1918, 309A.

[52] E. F. Kern, Amer. Elect. Soc., May 1918; *J.*, 1918, 423A.

Zinc production by electrolysis is making rapid strides forward. A new idea in this work is due to A. G. Betts,[53] who has introduced the method of "tank potential" for increasing the efficiency when depositing zinc from leach liquors in a lead-lined tank with electrodes of aluminium. The lead lining is connected through a resistance to the negative terminal so that the lead is maintained at a negative potential sufficiently high to prevent its solution; even a small amount of zinc may be deposited thereon. The discharge of hydrogen is suppressed and the presence of detrimental soluble lead salts is avoided.

An investigation of the conditions governing efficient zinc electrodeposition has been made, which shows the importance of removing foul electrolyte at intervals and also of keeping down the acidity in order to obtain a high yield of pure metal.[54]

For obtaining metallic zinc from "blue powder," a scheme has been patented by which the partially oxidised metal is treated with chlorine and the fused chloride electrolysed, or the powder may be briquetted and made the anode in a suitable electrolytic bath.[55]

It has long been known that a firm deposit of copper and other metals depends upon a low current density at the cathode, and a solution not too concentrated; the reverse of these conditions has been recommended for preparing metallic powder.[56]

Electro-thermal zinc processes have been rather out-classed by the rapid advance of electrolytic methods, but a new furnace is described,[57] of the resistance type, working at 1800° C., which is gas-tight during reduction, distillation, and condensation; these conditions should render possible the condensation to metal without the objectionable formation of large quantities of zinc dust. Another cell has been devised for producing zinc by electrolysing the fused chloride.[58]

Two new methods of dealing with gold and silver deposition are reported. One is a modification of the cyanide process, in which the pulped ore is agitated in the cyaniding vessel, and the mixture then run to a shallow electrolysing vessel which contains a number of vertical steel plate cathodes and tantiron anodes. Air agitation is employed in this tank, and the residual pulp is returned to the cyaniding vessel for further treatment.[59] In the other process the finely divided mineral is agitated with sodium chloride solution and electrolysed, the amount of salt used being proportional to the quantity of gold and silver present in the mineral.[60]

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[53] U.S. Pat. 1252654; *J.*, 1918, 155A.

[54] C. A. Hansen, *Met. and Chem. Eng.*, 1918, **18**, 481; *J.*, 1918, 338A.

[55] I. Partanen, U.S. Pat. 1254531; *J.*, 1918, 185A.

[56] W. C. Moore and others, U.S. Pat. 1254056; *J.*, 1918, 186A.

[57] H. Nathusius, *Metall u. Erz*, 1918, **15**, 87, 108; *J.*, 1918, 376A.

[58] J. L. Malm and others, U.S. Pat. 1255197; *J.*, 1918, 213A.

[59] A. A. Lockwood, Eng. Pat. 112876; *J.*, 1918, 154A.

A special arrangement of vats has been patented, applicable to the production of aluminium and other metals, in which the chief object seems to be the reduction of the quantity of conductors and leads required by arranging the vats in series system, but any one vat may be removed or repaired without interference with the working of the rest.[61]

Antimony.—A new method of dealing with stibnite appears to have met with success, since a yield [62] is reported of 1000 lb. per day of metal which assays 99·94%. The bath is composed of 7% sodium hydroxide and 2% common salt solution, in which the crushed ore is dissolved before being filtered into a wooden vat fitted with mild steel electrodes.

Iron [63] so far has been made in a pure state by deposition from chloride or fluoride solution, but a method is now suggested in which a slime is electrolysed which has been produced by fusing oxides of the metal with caustic alkali or alkali carbonate, and extracting with water.

Magnesium is evidently being dealt with in two ways. First by the contact cathode process,[64] and secondly by employing cathodes of molten tin, copper, or lead,[65] in both cases, of course, a molten magnesium salt is employed as electrolyte.

A new cell for the production of sodium from molten chloride has been patented, in which the cathodes are separated from the anodes by a metallic hood, which encloses the cathodes and also a pipe by which the liberated sodium is run off.[66]

ELECTRO-DEPOSITION. ELECTRO-TREATMENT.

For the deposition of metals by electrolysis it has long been the custom to employ solutions of complex salts, and Bancroft has stated that the tendency to form crystalline deposits decreases with the decrease in the concentration of the ions discharged.

During an investigation on this subject it has been shown that when silver is deposited from potassium cyanide solutions, its discharge is secondary and dependent upon the primary discharge of potassium. It is also apparent, from this work, that in order to produce a smooth amorphous deposit of any metal, another metal with a lower solution tension should be present.[67] A more concentrated cyanide bath than that generally employed is recommended by F. C. Mathers for copper plating.[68]

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[60] R. Reyes, U.S. Pat. 1243976; *J.*, 1917, 1278.

[61] C. H. Thomson, U.S. Pat. 1265551; *J.*, 1918, 474A.

[62] W. A. Burr, *Eng. and Mining J.*, 1917, 104, 789; *J.*, 1918, 11A.

[63] A. T. C. Estelle and others, U.S. Pat. 1275161; *J.*, 1918, 659A.

[64] Allgem. deuts. Metallwerk, Ger. Pat. 302024; *J.*, 1918, 339A.

[65] G. O. Seward and others, U.S. Pat. 1258261; *J.*, 1918, 272A.

[66] Badische Anilin u. Soda Fabrik, U.S. Pat. 1258529; *J.*, 1918, 272A.

The deposition of copper rings and bands is still receiving attention. In one case[69] the bands are deposited on a rotating cathode mandrel which is covered with alternating rings of lead and rubber, so that the copper bands are deposited upon the lead, and when sufficient thickness has been attained the bands can be easily removed from the mandrel. In another patent[70] the arrangements are somewhat similar, but burnishing of the bands is made possible during deposition, which gives a dense firm band or ring of copper suitable for the driving rings on projectiles.

The necessity for economy in platinum has brought about the construction of various electrode arrangements recently. The surface of a common metal may, for example, be coated with platinum by first rubbing it with a paste of ammonium platinichloride and potassium tartrate until sufficient platinum has been deposited, and it is then finished by making it the cathode in a bath of platinum chloride with a platinum anode.[71]

For zinc plating, Schoop's gas-heated " pistol " sprayer has been improved by utilising electrical heating. A short-circuit is formed between two zinc wires in the spraying " pistol, " and the molten metal is sprayed by a jet of compressed air.[72]

Electro-etching is evidently receiving attention. The plate to be etched has those parts which it is desired to protect covered with a suitable substance; it is then submerged in an electrolytic bath and made the anode. The electrolytes employed include oxalates, chlorides, and sulphates.[73]

Electrolytic pickling of steel is said to give a better surface than chemical pickling, and often in considerably less time.[74]

Electro-magnetic treatment of iron and its alloys previous to its use in transformers, &c., is said to improve the magnetic properties. The metal is subjected to alternate magnetising and demagnetising effects under reduced pressure or even at ordinary atmospheric pressure.[75]

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[67] R. S. Dean and M. Y. Chang, *Met. and Chem. Eng.*, 1918, **19**, 83; *J.*, 1918, 516A.

[68] Amer. Elect. Soc., May, 1918 *J.*, 1918, 423A.

[69] N. Huggins and others, U.S. Pat. 1268465; *J.*, 1918, 550A.

[70] E. G. Cook and others, U.S. Pat. 1271136; *J.*, 1918, 550A.

[71] B. B. Crombie, U.S. Pat. 1274995; *J.*, 1918, 623A.

[72] W. Kasperowicz, *Z. angew. Chem.*, 1918, **31**, 44; *J.*, 1918, 548A.

[73] U.S. Pats. 1275408 (W. S. Eaton), 1273432 (J. H. Weeks); *J.*, 1918, 593A, 659A.

[74] M. de K. Thompson and F. W. Dodson, *Met. and Chem. Eng.*, 1917, **17**, 713; *J.*, 1918, 92A.

Some recent work on the thermo-electric force of copper-nickel chromium alloys [76] has shown that such are suitable for thermo-couples, since they have a high melting-point and resist oxidation. The E.M.F. temperature-curves are approximately straight lines, and large variations in composition have little effect on the E.M.F.

Sparking plugs made of metals other than platinum claim attention on account of economy. Most of those devised are made of tungsten, molybdenum, or metals of the iron group; such are said to be more durable under the continual action of the spark [77] and have a very high welding point. In another spark plug, nickel, chromium, and manganese are alloyed.[78]

ELECTROLYSIS OF WATER. STERILISERS.

The production of electrolytic hydrogen and oxygen continues to call forth cells, mainly of the filter-press type, in which increased efficiency of working is combined with arrangements for preventing any possible mixing of the gases. The ease with which this type of cell may be built up to any size, and on the other hand dismantled for repairs and renewal of parts, is causing it to take a premier position amongst oxygen-hydrogen cells. The improvements relate principally to increased lightness of design, prevention of sagging of asbestos diaphragms, continuous supply of diluent to compensate for loss by electrolysis, and increased facilities for the assemblage and dismantling of parts.[79] The form of cell in which the anode surrounded by asbestos is suspended from the tank cover, has developed further into one from the cover of which anode and cathode are suspended together with the asbestos diaphragms which separate them.[80] Another cell[81] described is made up of two hemispherical sections clamped together by flanges separated by a non-conducting partition, on each side of which is a perforated disc electrode. This clamped flange construction is not new in electrolytic plant and sometimes provides a first-rate unit, for example in the Townsend cell for chlorine and alkali, but it will probably not prove suitable for electrolytic production of hydrogen and oxygen, especially in competition with the filter-press type, which is eminently suited for this particular work.

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[75] A. F. Berry, Eng. Pat. 118425; *J.*, 1918, 628A.

[76] M. A. Hunter and J. W. Bacon, Amer. Elect. Soc., May, 1918; *J.*, 1918, 424A.

[77] M. J. Insull, Eng. Pat. 113838; *J.*, 1918, 249A. G. A. Rignon, U.S. Pat. 1264685; *J.*, 1918, 428A.

[78] W. B. Driver, U.S. Pat. 1274395; *J.*, 1918, 628A.

[79] H. T. Shriver and J. McDougall, U.S. Pats. 1256067, 1269566, 1272397 1273357; *J.*, 1918, 249A, 593A.

[80] K. Kimura, Eng. Pat. 117533; *J.*, 1918, 552A.

[81] P. A. Emanuel, U.S. Pat. 1263314; *J.*, 1918, 380A.

An important departure in this class of production is the construction of cells for making electrolytic (detonating) gas for use in internal combustion engines. Obviously in constructing these cells every effort is made to assist the mixing of the hydrogen and oxygen, for which purpose the electrodes are generally disposed in a suitable mannner.[82] Perhaps water is to enter upon a new phase of its career as a power producer, for though the low efficiency of the steam-engine is well known, there seems to be every possibility that electrolytic gas power will show a very high efficiency. An ingenious method of decomposing water for this purpose depends on dropping acidulated water between spaced terminals which form a gap in an electrical circuit; the water bridges the gap and is electrolysed. The supply of drops and likewise the amount of gas may be regulated, and the arrangement seems well suited for use in conjunction with internal combustion engines.[83]

Another application of the electrolysis of water is for producing high pressures by electrolysing the water in a vessel completely filled with that liquid. One ampère-hour will give 624 c.c. of gas exerting a pressure of 1860 atmospheres, and this may prove to be of industrial value.[84]

Sterilisation of water by ozone or active oxygen has given rise to two new processes. In one, by an ingenious mechanical contrivance,[85] the water which enters operates an injector which draws air through an ozone generator. The water also raises a metal disc which closes the circuit so that a current is supplied to the ozoniser, and it then works on the vanes of a rotating interruptor. The electrolysis of water is employed in another process[86] in which the water flows through the anode compartment of a divided cell, to which carbon or manganese dioxide is added continuously, or instead, small granules of the substance may be used to line the anode chamber. Any iron and manganese in the water becomes oxidised and precipitated, whilst bacteria are destroyed by contact with the active carbon or peroxide surface.

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[82] C. F. Euler, Eng. Pat. 114491; *J.*, 1918, 311A. U.S. Pat. 1273050; *J.*, 1918, 570A.

[83] F. A. Osowski, U.S. Pat. 1259898; *J.*, 1918, 311A.

[84] K. Wilkens, *Chem.-Zeit.*, 1918, 42, 428; *J.*, 1918, 661A.

[85] L. H. E. Bégot and others, U.S. Pat. 1264360; *J.*, 1918, 440A.

[86] F. Tiemann, Ger. Pats. 301585, 302226, 302227; *J.*, 1918, 440A.

CHLORINE AND CHLORINE PRODUCTS.

The electrolytic production of chlorine demands much consideration at the present time. The gas has played a most important part in war-chemistry during the past four years, and the view is now generally held that the success of the process depends rather upon the market value of the gas than upon its more valuable partner, caustic soda; that is to say, cheap chlorine will decide how far electrolytic chlorine and caustic soda plants can be run successfully.[87] The cells brought out recently are built on the Hargreaves-Bird pattern, and no doubt this type has very much to recommend it.[88]

A cell has been devised for producing chlorohydrocarbons simultaneously with caustic soda, by admitting suitable gases to the anode compartment, so that they react with the chlorine as rapidly as it is discharged. If the reaction is conducted at a temperature of 97°–100° C., olefinic hydrocarbons yield chlorhydrins.[89]

Chlorine gas may be recovered from gaseous mixtures by washing them with ferrous chloride solution; this treatment produces ferric chloride, which is acidified with hydrochloric acid and electrolysed. Chlorine in a concentrated form is generated at the anode, and the ferrous chloride formed simultaneously at the cathode is passed out to wash the gas mixture.[90]

A cell suitable for making chlorates and perchlorates has been patented, the construction of which, it is claimed, obviates, entirely or partially, the expense of platinum electrodes.[91]

VARIOUS INORGANIC PRODUCTS.

No great activity has been displayed in this province during the past year. The preparation of certain per-salts has received attention, and the remaining work in this particular domain relates to the preparation of alkali salts from natural silicates and the regeneration of certain liquors by electrolytic oxidation or reduction.

Potash may be produced from felspar[92] by mixing the ground silicate with carbon in the anode compartment of a divided cell. The electrolyte is hydrofluoric or fluosilicic acid which, during electrolysis, attacks the silicate, forming potassium fluoride or fluosilicate. At the cathode

[87] V. R. Kokatnur, *Chem. and Met. Eng.*, 1918, **19**, 667.

[88] N. Statham, Eng. Pats. 114974, 118355; *J.*, 1918, 380A, 706A.

[89] K. P. McElroy, U.S. Pats. 1264535, 1264536; *J.*, 1918, 416A.

[90] P. L. Hulin, U.S. Pat. 1246099; *J.*, 1918, 57A.

[91] T. G. Hitt, U.S. Pat. 1256319; *J.*, 1918, 249A.

[92] E. L. Anderson, U.S. Pat. 1253560; *J.*, 1918, 149A.

caustic potash is formed. Another process for breaking up insoluble silicates is a modification of the Lawrence Smith fusion method in which electrolysis is employed to regenerate the chlorine and reproduce calcium chloride for the fusion. Briefly, after fusion of the silicate with lime and calcium chloride, the extracted potassium chloride is electrolysed and the resulting chlorine is passed into a mixture of potassium chloride and lime; part of it is utilised in transforming the former into chlorate, and the lime is converted into chloride.[93]

Perborates[94] are made by electrolysing a mixture of alkali borate and carbonate. It has been found that it is desirable to keep the solution saturated with both salts, and to employ a current density which is approximately the same at anode and cathode. The reducing action of the cathode may also be diminished by the addition of alkali chromate to the solution.

The yield of potassium persulphate[95] is said to be increased considerably if, when electrolysing acid potassium sulphate under proper conditions, some ammonium or sodium bisulphate be added.

Perchloric acid[96] may be prepared by electrolysing a solution of hydrochloric acid of not greater than normal concentration. The current density employed is 0·5 ampère per sq. cm., temperature not above 50° C. at first, being subsequently lowered, and a continuous flow of electrolyte is maintained during the initial stages. A concentration of 60% of perchloric acid is ultimately obtained.

Stannous chloride solution may be regenerated by electrolysis in a diaphragm cell constructed to facilitate the removal of discharged chlorine.[97]

An improvement has been patented for the regeneration of chromic acid,[98] in which copper sulphate is included in the electrolyte, with copper-plate cathodes and lead peroxide anodes. A small quantity of copper in the regenerated liquor does not impair its value as an oxidant of organic substances.

Electrolytic precipitation of substances from solution by the anodic corrosion method (pigments, &c.) has not figured prominently, but a process has been patented for producing metallic sulphides by this means, in particular, antimony sulphide. One patent appears to cover nearly all possible variations of carrying out the process, the best of which is probably the one in which a stibnite cathode is employed with an antimony anode in a solution of common salt.[99]

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[93] J. S. Beckett and P. R. Moses, U.S. Pat. 1247619; *J.*, 1918, 56A.

[94] O. Liebknecht, U.S. Pats. 1253060, 1253061; *J.*, 1918, 150A.

[95] Neher & Co., and O. Nydegger, Ger. Pat. 306194; *J.*, 1918, 581A.

[96] E. C. Walker, U.S. Pat. 1271633; *J.*, 1918, 580A.

[97] Siemens und Halske A.-G., Ger. Pat. 302040; *J.*, 1918, 334A.

[98] P. Goldberg, Ger. Pat. 303165; *J.*, 1918, 334A.

Fractional deposition of the rare earth hydroxides has been further studied by L. M. Dennis[100] and his co-workers, who have shown that by electrolysis of neutral solutions of the rare earth nitrates, these hydroxides are precipitated at a mercury cathode in order of their basicity. A point of practical value is that the percentage of thoria in rare earth mixtures can be greatly increased by the process. Ceric oxychloride[101] is deposited as a dark brown mass on the anode by electrolysing fused cerous chloride containing a small amount of moisture; examination of the product showed it to be contaminated with ammonium chloride.

Amongst special products the following should be mentioned: Endothermic gas reactions, such as oxide of nitrogen formation, can be brought about with great efficiency if, in a Pauling type of furnace, cool air be admitted in such a manner as to cool the gases rapidly, immediately they leave the arc.[102] Reduction of tungstic oxide may be effected in a silica tube resistance furnace, provided it be protected from suboxide attack by a thin lining of nickel.[103] Crystalline alumina can be more efficiently made in the hearth of an arc furnace if the hearth be covered with a layer of oxidised substance which yields volatile reduction products (zinc oxide, soda ash); these prevent the alumina from coming into contact with the carbon hearth and so being reduced.[104]

PRODUCTION OF ORGANIC COMPOUNDS.

Comparatively little work has been recorded in this sphere. According to an American investigator,[105] synthetic gasol ne may be produced by subjecting heavy hydrocarbon vapours, mixed with methane, to the electric discharge of a high tension current of high frequency. Kerosene, for example, mixed with natural gas, gives a large percentage of oil boiling between 45° and 160° C. It is hoped, ultimately, to attain a yield of 100% of such oil at an energy cost of 0·4 cent per gallon.

Sugar refining by electrolysis has been under consideration for some time. In a new process the impurities in the juice which are susceptible to electrolytic action are made to pass through porous partitions, some to the anode and some to the cathode compartment, which is situated at one end, and adjacent to the central compartment containing the sugar juice.[106]

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[99] C. O. Griffith, Eng. Pat. 113508; *J.*, 1918, 212A.
[100] *J. Amer. Chem. Soc.*, 1918, **40**, 174; *J.*, 1918, 123A.
[101] H. Arnold, *Z. Elektrochem.*, 1918, **24**, 137; *J.*, 1918, 505A.
[102] R. Pfaehler and others, U.S. Pat. 1249479; *J.*, 1918, 96A.
[103] M. J. Insull, Eng. Pat. 113839; *J.*, 1918, 248A.
[104] R. H. White and others, U.S. Pat. 1269141; *J.*, 1918, 545A.
[105] L. B. Cherry, Amer. Elect. Soc., Oct., 1917; *J.*, 1917, 1266.

The production of *p*-aminophenol has long interested electrochemists, and T. Shōji[107] has investigated Gattermann's original method in which nitrobenzene is electrolysed in a cathode compartment containing 80% sulphuric acid. He has found that vigorous agitation is essential for success, and claims that, with a yield of 43%, the process should compete with the purely chemical one on account of simplicity, which seems quite reasonable. This is only one of the many organic electrolytic reduction processes likely to be utilised commercially.

A matter of more academic interest is the electrolytic production of esters of nitrobenzoic acid at the anode, by electrolysis of a mixture of the potassium salt of this acid and the free acid, together with acetic anhydride.[108] Nitrobenzene and *o*-nitrophenol are formed simultaneously.

ELECTRIC FURNACES.

The amount of activity displayed in this branch of work has been very considerable during the past year. Many new furnaces have been devised, older patterns have been modified, and special attention has been devoted to the composition of electrodes and methods of controlling their positions. The automatic control of temperature in both arc and resistance furnaces has been extensively dealt with.

Further, many improvements have been introduced in connection with the arc welding of metals and the arc deposition of refractory metals, whilst in a few cases the production of particular substances occupies a more prominent position than the furnaces in which such processes are conducted.

The arc furnace will be considered first, as this has occupied more attention than the other types. The arc furnaces are not generally allocated to any particular purpose, but improvements have been introduced to increase the efficiency of this valuable adjunct of the metallurgical industry which is now widely utilised in the production of ferro-alloys and steel.

The Booth-Hall[109] furnace of the vertical arc, conducting hearth

[106] R. R. Williams, U.S. Pat. 1256758; *J.*, 1918, 255A.

[107] *J. Chem. Ind. Tokyo*, 1918, 21, 117; *J.*, 1918, 459A.

[108] C. Schall, *Z. Elektrochem.*, 1918, 24, 154; *J.*, 1918, 530A.

[109] W. K. Booth, Amer. Elect. Soc., May, 1918; *J.*, 1918, 422A.

type, and the vom Baur[110] furnace have been fully described by the inventors. The Héroult furnace for steel castings is stated to give a greater output if the copper spacers between the bus-bars are replaced by "vulc-asbestos" spacers, and the bus-bar leads insulated from each other by mica.[111]

In most cases the improvements relate to the disposal of electrodes, which are arranged to obtain the maximum heating effect, efficient circulation of the molten metal in the furnace, and decrease of wear and tear on the lining.[112]

For the electrical reduction of ores an arc may be formed between electrodes embedded in the crushed ore, but two balancing electrodes are fixed in the side of the furnace, so that if the resistance of the smelt mixture becomes too great, the current passes to the balancing electrodes instead of to the lining, which is by this means preserved.[113] In another furnace supplied with three-phase current, there are three upper electrodes and three lower electrodes so arranged that a good distribution and control of heat are attained and thorough mixing of the molten charge is assured.[114] In another type, circulation is produced by connecting the neutral point of the secondaries of the transformers to the steel shell of the furnace.[115]

Three-phase current is generally employed in furnace work, and an effort has been made to distribute the current so that the loads on the several phases are balanced in such manner that the heat may be regulated without seriously disturbing the supply system.[116] According to another patent, it is possible to construct the furnace support in such a manner that in tilting for pouring purposes the receiver always occupies the same relative position to the pouring spout; at the same time the furnace floor is concave in shape, so that the length of arc is not altered by tilting.[117]

In another furnace for melting non-ferrous alloys,[118] the crucible is surrounded by broken coke so that the arc may be struck through the coke packing instead of through the molten alloy, which has a lower resistance and consequently does not give much heat.

The melting of brass in electric furnaces has presented many difficulties, and as a result of an investigation by the United States Bureau of Mines, a rocking furnace suitable for the work has been devised. It takes the form of a drum 5 ft. in length and 5 ft. in diameter, and has a capacity of 1300 lb. per two hours.[119]

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[110] J. vom Baur, Amer. Elect. Soc., May, 1918; *J.*, 1918, 422A.

[111] R. F. Flinterman, Amer. Elect. Soc., March, 1918; *J.*, 1918, 421A.

[112] O. Sahlin, Eng. Pat. 115719; *J.*, 1918, 381A.

[113] B. G. Cobb and others, U.S. Pat. 1267976; *J.*, 1918, 551A.

[114] British Electric Transformer Co. and F. E. Berry, Eng. Pat. 115247; *J.*, 1918, 380A.

[115] W. E. Moore, U.S. Pat. 1272077; *J.*, 1918, 592A.

[116] W. Travis and Watson & Co., Eng. Pat. 118233; *J.*, 1918, 591A.

[117] F. T. Snyder, U.S. Pat. 1254077; *J.*, 1918, 186A.

[118] V. C. Faulkner, Eng. Pat. 115248; *J.*, 1918, 378A.

In a discussion on electric furnaces arranged by the Faraday Society in February 1918, it transpired that resistance and arc furnaces are in most favour, whilst there is a strong demand for a suitable electrically fused refractory lining.

The principle of motor control for the adjustment of the relative positions of electrodes[120] is being extended. In one type in which a fixed electrode is situated in the base of the furnace, two adjustable electrodes are arranged vertically above; one of these is attached to a motor for adjustment in response to variations in current, whilst the other is adjusted by another motor which responds to variations in voltage.[121]

A system of electro-magnetic control has been arranged for two-phase supply, whereby the common return electrode is adjusted independently of the other two, an improvement on the arrangement by which all three are raised or lowered together.[122]

The electrodes (generally of carbon) oxidise to a considerable extent on being withdrawn from the furnace, and this may be avoided by the construction of suitable coverings devised to keep the air from the heated electrodes on their withdrawal from the furnace.[123] A good deal of trouble has been experienced in the past in clamping electrodes firmly in holders so that they remain well fixed even when heated. A special holder has been devised to overcome this defect.[124]

Electrodes for arc welding or soldering continue to be devised. In one of these the electrode is twisted, or has a screw thread cut on it; this is claimed to burn away regularly, and the slag protector does not peel from the electrode so easily as in the case of ordinary plain electrodes.[125] In another patent the electrode tip is coated with a metal of low melting-point in order to ensure good contact with the work and so avoid burning.[126]

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[119] H. W. Gillett and A. E. Rhoads, *Met. and Chem. Eng.*, 1918, **18**, 583; *J.*, 1918, 423A.

[120] Brown, Boveri & Co. and A. Gray, Eng. Pat. 113827; *J.*, 1918, 249A.

[121] J. A. Seede and A. D. Keene, U.S. Pats. 1253732, 1255613; *J.*, 1918, 156A, 213A.

[122] J. L. Dixon, U.S. Pat. 1248632; *J.*, 1918, 62A.

[123] W. B. Hamilton and J. Holland, Eng. Pat. 115705; *J.*, 1918, 381A. J. R. Hoyle and P. Fawcett, Eng. Pat. 114395; *J.*, 1918, 273A.

[124] P. Fischer, U.S. Pat. 1259842; *J.*, 1918, 311A.

[125] A. B. Pescatore, Eng. Pat. 118296; *J.*, 1918, 628A.

[126] J. H. Gravell and others, U.S. Pat. 1267400; *J.*, 1918, 551A.

An interesting extension of electric welding is the electro-deposition of metals,[127] particularly the constituents of high-speed steel, one electrode of the arc being composed of the mixture which it is desired to deposit or "splash on."

Resistance furnaces have been improved, mainly by adjusting the position and shape of the resistor and also by modifying its composition. Silicon carbide has been found a very durable resistor.[128] A resistance furnace suitable for melting brass has been devised.[129] The placing of the resistor above the level of the hearth is advocated, the heat being reflected down from the roof on to the hearth.[130]

An interesting combination of two furnaces has been described, in which current from three-phase supply is employed, the current being supplied to the resistors in such a manner that one furnace has a temperature twice as high as the second.[131] A small experimental furnace has been constructed in which the graphite resistor takes the form of a tube made up of rings fitting one into the other. One such furnace gave 100 heats during six weeks at a temperature of 1800°–2400° C. with very little repair.[132] According to another patent, zirconia can be employed as a resistor provided it is first heated by a surrounding shell to a sufficiently high temperature.[133]

The induction furnace is subject to considerable energy losses unless the positions of primary and secondary windings are rightly adjusted. A special arrangement, in which heating at the lowest part is combined with full utilisation of the "pinch effect," assists circulation and consequently conservation of heat.[134]

ELECTRO-ANALYSIS.

Analysis by electrolysis continues to make progress. During the last few years several important separations have been introduced, and G. L. Kelley and his co-workers in America have done considerable work upon the electrolytic determination of metals as applied to steel analysis. Manganese may be estimated, in the presence of chromium and vanadium, by reducing the permanganate (formed by the persulphate method) with mercurous nitrate, the end point being judged by the electrometric method—that is, by noting the sudden change of E.M.F. of a suitable cell. In one form the beaker which contains the solution to be titrated is provided with a platinum electrode, and the solution communicates by a capillary tube with a solution of potassium nitrate containing a calomel electrode; changes of potential are detected by a galvanometer. The process just described was used particularly for titrating vanadate solutions with ferrous sulphate.[135]

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[127] E. H. Jones, Eng. Pat. 116308; *J.*, 1918, 473A.

[128] F. Thornton, Amer. Elect. Soc., Oct., 1917; *J.*, 1917, 1279.

[129] T. F. Baily, Amer. Elect. Soc., Oct., 1917; *J.*, 1917, 1276.

[130] T. F. Baily and others, U.S. Pat. 1272186; *J.*, 1918, 592A.

[131] T. F. Baily and others, U.S. Pat. 1260298; *J.*, 1918, 312A.

[132] W. Rosenhain and E. H. Coad-Pryor, *J.*, 1918, 156A.

[133] G. B. Filmer and J. J. Denton, Eng. Pat. 112177; *J.*, 1918, 96A.

[134] C. B. Foley, Eng. Pat. 114853; *J.*, 1918, 308A.

The electrometric method of judging end points has also been developed by H. S. Harned and his co-workers, who claim that the method is especially suitable for the titration of dibasic acids and their acid salts.[136] It may also be employed in estimating certain divalent metals with standard sodium hydroxide; for example, magnesium, copper, nickel, and cobalt.[137]

In many cases of electro-analysis it is possible to dispense with platinum electrodes, since a copper cathode may often be employed, and an anode of graphite or, occasionally, some suitable metal.[138]

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[135] *J. Amer. Chem. Soc.*, 1916, **38**, 341; *J.*, 1916, 966. *J. Ind. and Eng. Chem.*, 1917, **9**, 280; 1918, **10**, 19; *J.*, 1917, 1011; 1918, 92A.

[136] *J. Amer. Chem. Soc.*, 1918, **40**, 1213; *J.*, 1918, 653A.

[137] H. S. Harned, *J. Amer. Chem. Soc.*, 1917, **39**, 252; *J.*, 1917, 355.

[138] T. Batuecas, *Anal. Fis. Quim.*, 1916, **14**, 495; *J.*, 1917, 355.

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OILS, FATS, AND WAXES.

By Cecil Revis, and E. R. Bolton, F.I.C.,
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General.

The past year, like the previous year, has not been fruitful in analytical processes or of the pure chemistry of oils and fats. This is only to be expected, as the conditions referred to in the Annual Report for 1917 continue, and have even been accentuated in their adverse effect on investigation. Many new sources of oils and fats have been examined, but probably at the moment little can be done to exploit any such new sources, as the importation of consignments of any magnitude into the country has not been allowed—a state of affairs which is likely to change for the better with increase of shipping facilities. This, however, has not hindered the consideration of these new fields and of the possibilities of developing the resources of various districts which hitherto have not very greatly added to the supply of raw materials. For this reason it has been considered advisable to allot a section to the consideration of literature which has been published during the last twelve months in various consular reports, trade journals, &c., as collecting together information which may possibly be of interest to those concerned with the development of new sources of raw material.

The bright hopes of the development of the edible oil industry in Great Britain which were indulged in during the early part of the year, have unfortunately not been as yet fully realised, and the industry is not in as satisfactory a state as might be desired. There is probably no industry which it was so necessary to foster as this one, as the sources of supply of the raw material lie so much in British Dependencies, and it is vitally necessary that this country be able to deal with the supplies so furnished, and to become the actual manufacturer of the refined products—an industry which hitherto has been largely in German hands—and to stop the diversion of these supplies of raw material to other countries.

No doubt the shortage of shipping capacity has necessitated some of the difficulties, but there is no doubt that, properly fostered, the edible oil refining industry may attain a very strong position when normal conditions begin to prevail again.

The plan of last year's Reports has been followed in dealing with both analytical methods and with special oils and fats. These latter are always worthy of careful consideration, as many of them bid fair to take a prominent place in the near future. It would be of great assistance if investigators, when examining new sources of fats and oils, were to ascertain, as far as possible, the extent of the supply, and its relation to means of transport. There have been many valuable oleaginous seeds described from time to time, which have raised hopes of great utility, but which on investigation have been shown to be the products of widely scattered trees, or else so far removed from shipping facilities as to be unremunerative if marketed. Many factors enter into the question of a satisfactory return, one of the most important being probably the supply and cost of labour and collection. For instance, these two factors have been the great barriers in the way of the remunerative working of the palm oil industry, and though some endeavours are being made to obviate these, they still require the utmost consideration in the development of the new fields of supply. In the keen competition of the next few years, these methods, together with those of preparation for transport, will become of great moment, and provide much opportunity for commercial enterprise.

Commercial Development in the Oil Seed Industry.

Cotton Seed Products.

Cotton seed oil has always been looked upon as a most useful oil on account of its cheapness, but its ability to compete in the market has largely depended on the value of the cake. With the increase in demand for cotton from within the British Empire will come the problem of economically dealing with the by-products, viz. the oil and the cake. That we are much behind the times in these respects is undoubted, and there is a very great necessity for attention to be paid to them. For this reason two articles which have appeared in the Journal are worthy of the closest attention. These are entitled "Some cotton seed products in their relation to present day needs," by E. C. de Segundo,[1] and "Cotton seed products and the chemical industries," by E. Thompson,[2] and both deal with the various aspects of the question.

There is no doubt that American cotton oil has been vastly ahead of the home production, and the reasons for this are very carefully enumerated in the former of these articles. With regard to cotton oil, it may be noted that from January 1, 1918, American refiners have agreed to purchase and sell all oil on the "pound" basis in contradistinction to the old practice under which the crude oil was sold on a "gallon" basis, and the refined product on the "pound" basis.

CASTOR OIL.

This oil has achieved a prominence hitherto unknown on account of the demand made for it as a lubricant in aeroplane machinery. As to a certain extent such a use will continue in normal times, much interest attaches to the attempts which are being made to increase cultivation and output. This is well illustrated by the fact that whereas the British production in 1915 was about 10,000 tons per annum, this has risen to a figure nearer 200,000 tons at the present time. To meet these demands attempts are being made to plant Indian seed in the Southern States of America and on the Pacific Coast. Brazil is showing very favourable returns, and China and South Africa will soon come into the market. The Dominican Republic is also giving every facility and help to farmers to cultivate the bean, as a very good type can easily be grown and the crop is heavy. Given favourable conditions, the beans grow easily and achieve maturity in three to four years, the best results being obtained from *Ricinus sanguinensis*. Siam is also undertaking the proper cultivation of the plant which hitherto has only grown wild. Many of these districts are installing crushing machinery, and in fact this must eventually be the case with any district which desires to compete in the world's markets, as the useless character of the cake precludes the economical shipment of the whole beans. Details of these developments will be found in the United States Consular Reports, February 23, July 20, 1918.[3]

MISCELLANEOUS SEED CROPS.

***Bean Oil* (*Soya*).**—The Report of H.M. Consul in Darien states that a company was formed in Manchuria in 1918 for hardening bean oil, and that the start up has been so far successful. The company is producing pure and crude glycerin as well as the hardened oil.

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[1] *J.*, 1918, 118T.

[2] *J.*, 1918, 166R.

[3] *J.*, 1918, 153, 364, 366R.

Coconut Shells.—The U.S. Consular Report for March 7, 1918,[4] draws attention to the waste of fuel which takes place in the improper use of these shells. A suggestion is made to briquette these for export, and the following data are quoted with regard to their value, viz. for a 12-hour run, 1200 lb. shell and 600 lb. coal = 1900 lb. coal + 150 lb. wood = 4000 lb. wood + 400 lb. coal.

Grain Germs.—The difficulties of the German Empire have caused their Committee on Oils and Fats to utilise the germ of grain as a source of oil. These germs contain 10 to 12% of oil, and in nine months about 4000 tons was obtained. The press cake naturally is a valuable foodstuff.[5]

Maize Oil.—This "germ oil" is through the pressure of circumstances being made great use of in Hungary. The mills in Roumania have been largely used, one alone producing 200 tons per week. Apparently very large quantities would be available if all the Roumanian crop were dealt with.

Sesamé Oil.—The yield of sesamé oil and acreage under cultivation in British India show a considerable decrease during this year.[6] This is probably largely due to the closing of the German market, as the seed was little utilised before the war, though during the past year a fair quantity of sesamé seed has been crushed in the United Kingdom, and the oil refined for margarine purposes. It has proved remarkably successful for this purpose, and the product has been good, though it is quite a new experience for most English refiners.

Tomato Seed Oil.—Italy at the moment is producing about 600 tons per year of oil from this source in the province of Parma, this being the output from about 84,000 tons of the fruit. Attention has been drawn under "Tomato seed oil" (see Special Oils) to the possibilities of this oil in America.

Walnut Oil.—Some statistics are available with regard to the war production of this oil in Germany. In the year 1917–18, 7700 cwt. of walnuts were collected by the authorities, from which about 1078 cwt. of oil was obtained.[7] It is proposed to use this oil in margarine, but the result would scarcely be satisfactory, as walnut oil is not suitable for this purpose.

Whale Oil.—The Norwegian Government has been giving much attention to whale oil for margarine purposes. The earlier attempts at deodorising the oil were a failure, as the fishy taste returns very readily, as is the case with most fish oils. Hardened whale oil is satisfactory in this respect, but until lately the hardening process had to be carried so far that the fat became unsuitable. This Government now reports that a satisfactory product is being made without excessive hardening.[8] There is no doubt that whale oil is a most suitable fat for margarine if it can be brought into a satisfactorily stable condition, and this new hardened product may have a considerable future before it.

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[4] *J.*, 1918, 228R.

[5] *Bd. of Trade J.*, Feb. 21, 1918; *J.*, 1918, 96R.

[6] *Indian Trade J.*, Jan., 1918; *J.*, 1918, 135R.

Bd. of Trade J., Apr. 11, 1918; *J.*, 1918, 155R.

OIL INDUSTRY IN VARIOUS COUNTRIES.

China.—A report has been published on the resources of the Yunnan Province with regard to oleaginous seeds. Colza appears to be the principal product, but the yield of oil owing to crude native methods is not good. Rape seed is available up to several thousand tons per annum. Sesamé, arachis, and castor seeds are also produced, but the quantities are small. An export duty is levied on these seeds.[9]

Indo-China.—The possibilities of obtaining many oleaginous seeds from this district seem to be great. The seeds available at the moment are cotton, soya, castor, sesamé, and peanut, together with copra. The oil content of many of these appears to be well above the average. For instance, sesamé is grown with 50% of oil, and a yield per acre double that of British India. Fairly heavy yields per acre of peanut are recorded. Naturally Marseilles will be the chief importer of the produce of Indo-China, but the records of crop production, especially in regard to soil composition, are of general interest.[10]

India.—It may be noted that a first shipment of shelled ground nuts of 2424 tons has been made this year from Madras to the United States. There is no doubt that this method of shipping ground nuts will steadily increase, as the bulk is greatly diminished thereby. The Bombay Presidency, in the year 1916–17, produced 208,000 tons of these nuts, a good deal being pressed locally, as the cake was largely exported to England before the war.[11]

Japan.—This country hitherto has played little part in the export of vegetable oils, but there is reason to believe that the future will see her entry into the world's markets. Possibly the chief oil for some time will be soya oil, as the raw material is plentiful, and a company has been formed to manufacture the refined product. It will be interesting to note what the new Japanese company can do in this direction, as soya oil is rather the bugbear of the refiner, the stability of the product being somewhat uncertain, and in this country it is rather regarded as a "technical" oil.[12] The returns for the last two years of the Kobe factory show a very successful output of soya, coconut, rape, cotton, and nut oils. Much of the machinery is up to date in this district, and is largely obtained from America. There appears to be great activity in the district in order to supply the demand for oils in America.[13]

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[8] *Chem. Umschau*, No. 12, 1917; *J.*, 1918, 115R.

[9] *J.*, 1918, 343R.

[10] *J.*, 1918, 247R.

[11] *Bd. of Trade J.*, Sept. 12, 1918; *J.*, 1918, 384R.

France.—The after-war situation is discussed in *Chimie et Industrie*, August 1918,[14] in view of the altered conditions. It is anticipated that the British demand for much of the raw material from her own colonies, hitherto diverted to France, will have to be met by development of French colonial resources. The chief difficulty will probably arise from shortage of copra. Nut oil, palm and palm kernel oils will, however, be supplied in sufficient quantity from French West Africa, and this source could be developed. It is also intended to cultivate castor seed in Madagascar and Africa. The enormous demand of Marseilles alone may be gathered from the fact that in 1910 the tonnage of oil seed imports was 665,679, but this has fallen steadily during the war. In 1916, 224,087 tons of ground nuts and 105,763 tons of copra were imported.

Rhodesia.—Here also the promise of the future seems hopeful. So far sunflower and arachis seeds are the only commercial products, and everything should be done to encourage the former, at any rate, as the oil is a valuable one, and the cake also. Too little has been done hitherto in this direction, as the sunflower grows with great facility. Experimental plantings of castor, sesamé, and linseed have been made, and the results so far are satisfactory. For the proper exploitation of sunflower seed it may be noted that crushing should be carried out and the cake used locally. It may not be possible to export the seed itself profitably.[15]

GENERAL CHEMISTRY.

The year's literature shows very little work dealing with the general chemistry of oils and fats. The adverse causes noted in last year's reports still operate, possibly more strongly than ever, and the result is seen in the paucity of papers published. In dealing with work on the general chemistry of this subject, it is somewhat difficult to draw the line between matter which should be classified as pure chemistry and that which is rather of the analytical type. For this reason some of the papers which might be included here have been dealt with under the heading of Analytical Chemistry, as the results have a more direct bearing on practice. The record of work is too heterogeneous to be treated as a whole, and the papers are noted under separate headings.

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[12] *J.*, 1918, 287R.

[13] U.S. Cons. Report, Sep. 4, 1918.

[14] *J.*, 1918, 380R.

[15] *J.*, 1918, 224R.

Sulphonation of Oils.—The reaction taking place during sulphonation of fixed oils has always been a somewhat vexed question, and for this reason a paper by L. G. Radcliffe and S. Medofski[16] is of interest, particularly as the authors preface their work with a good summary of earlier work. The experiments were partly directed to the examination of the fatty acids present before and after sulphonation, in order to determine the changes which take place in them. The results with cotton seed, olive, and sesamé oils point to polymerisation, as the neutralisation value decreases, together with the iodine value, while the solidification temperature is increased. There is also evidence of the formation of hydroxyl groups. This last does not seem to occur with rape and whale oils Linseed oil, on the other hand, appears to undergo little change. Castor oil polymerises without formation of hydroxy-compounds. The ease with which sulphonation takes place is stated to depend on the percentage of olein present in the oil, which is said to be converted into such saturated compounds as θ-tri-olein hydrogen sulphate and *i*-tri-olein hydrogen sulphate, these saponifying easily and forming hydroxy acids, the θ-form of which is further changed to lactones. The experiments are to be developed with tung oil.

Drying Oils.—R. S. Morrell[17] publishes the results of an extended investigation into the cerous salts of the fatty acids, and their bearing on the action of cerous salts as driers. The general type of salt found is represented by the formula CeX_3, where $X =$ the acid radicle. The cerous salts of the saturated acids were found to be insoluble in ether, whilst those of the unsaturated acids were soluble, but the solutions darken on exposure to the air, and in the case of linolenic acid deposited a buff-coloured precipitate having a peroxide reaction. The composition of the precipitate corresponded to the formula $CeO(XO_2)_2$, due to oxidation of the form CeX_3, which latter is found in the solution with the form CeX_4.

It was hoped that the differences in solubility in ether of the various cerous salts might lead to useful information on the change of linking, which it is maintained takes place during thickening. From olive and poppy seed oils the types CeX_4 and $Ce(OX)_2$ were obtained. The effect of oxidation, however, appears to play a considerable part in the changes taking place, but it would seem that support has been advanced in favour of the view that a change in the internal linkages is a prelude to polymerisation. The rate of absorption of oxygen by cerous α-elæostearate has been studied, and the primary oxidation takes place fairly rapidly, resulting in the form $Ce_2O(XO_2)_6$, but the second double linkage is only peroxidised after a year's exposure to oxygen. The author advances the view that with drying oils the oxidation to peroxidic acids is the prelude to polymerisation, and accounts in this way for the need of two different driers, one of which is essential to oxidation, whilst the other accelerates the polymerisation change.

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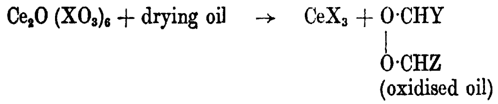
[16] *J. Soc. Dyers and Col.*, 1918, **34**, 22; *J.*, 1918, 157A.

[17] *Chem. Soc. Trans.*, 1918, **113**, 111; *J.*, 1918, 130A.

The oxidation of cerous α-elæostearate is represented by the following scheme:

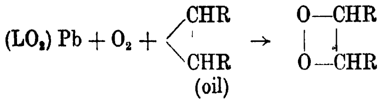
$$CeX_3 \rightarrow Ce_2(XO_2)_6$$



$$Ce_2O(XO_3)_6 + \text{drying oil} \rightarrow CeX_3 + \begin{array}{l} O{\cdot}CHY \\ | \\ O{\cdot}CHZ \end{array}$$

(oxidised oil)

With this may be compared the scheme of Ingle [18] for lead linoleate:



$$(LO_2)\,Pb + O_2 + \left\langle \begin{array}{l} CHR \\ | \\ CHR \end{array} \right. \rightarrow \begin{array}{l} O{-}CHR \\ |\quad\;\; | \\ O{-}CHR \end{array}$$

(oil)

The author notes that there is practically no change of the α-elæostearic acid into the β-variety during the above-mentioned changes, but in a later paper [19] he shows that when methyl α-elæostearate is distilled, a very large conversion into β-methyl ester occurs, and that this takes place during the distillation and not during the preliminary thickening of the oil.

The commercial production of fats by synthetic methods is discussed by R. J. Moore and G. Egloff,[20] who draw attention to the various methods which have been proposed from time to time for the conversion of hydrocarbons of the paraffin, olefine, and naphthene series into fatty acids. The question may be interesting from a scientific point of view, but though fatty acids are produced, these are not fats, and though the authors believe that the synthetic production of fats may possibly be realised in the near future, any such methods will have a serious competition in the vast stores of vegetable fats which are as yet almost untouched.

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[18] *J.*, 1917, 319.

[19] *J.*, 1918, 181T.

[20] *Met. and Chem. Eng.*, 1918, 18, 308; *J.*, 1918, 232A.

It is not out of the way to draw attention to the work of F. Hulton-Frankel,[21] who has followed up the work of Falk[22] on the power of proteins to acquire ester-hydrolysing properties in presence of alkali. As a very large number of plant proteins such as phaseolin, castor-bean, and soya-bean globulins, &c., and also casein, are now shown to acquire such properties, the fact that the ester-hydrolysing property is not destroyed by boiling may possibly have some slight bearing on the question of production of free fatty acidity and rancidity under certain conditions.

Special Oils and Fats.

As in the Reports for 1917, the various oils and fats which have been investigated are collected as far as possible under headings. The work done in this direction during the past year is characterised in many directions by being the result of necessity and of the utilisation of waste products, which have hitherto not been regarded as commercially valuable. It will remain to be seen whether many of these expedients will survive the competition of ordinary oleaginous products.

Butter Fat.—It may be noted that A. Seidenberg[23] has applied his method of crystallisation from a mixed solvent by gradual elimination of the more volatile constituent[24] to the detection of foreign fats in butter. The method may be of interest to some, but it would need very careful investigation before reliance could be placed on it, as it necessarily will suffer from the same deficiencies as other turbidity methods which have been devised for the examination of butter fat.

Coconut Oil.—A valuable series of articles dealing with coconut oil and copra is contributed by H. C. Brill and co-workers.[25] The ground covered is extensive, and almost every aspect of the commercial use of the coconut dealt with. The methods of drying employed in the Philippines are considered, and their defects criticised, as the endeavour is to produce locally oil comparable with the best Cochin oil. In this connection sulphur dioxide has been employed to destroy moulds. The deterioration due to this cause is the subject of another section of this communication, and the connection between moisture and mould growth has been investigated. The most serious loss of oil arises from the action of varieties of *Aspergillus*, whilst *Penicillium* does not appear to be so destructive. It is necessary that the copra be dried down to a maximum water content of 6%, and it is pointed out that the inefficient native methods do not achieve this. There appears to be a decided opening for the introduction of drying machines, though there is much local prejudice.

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[21] *J. Biol. Chem.*, 1917, **32**, 395; *J.*, 1918, 135A.

[22] *J.*, 1917, 974.

[23] *J. Ind. Eng. Chem.*, 1918, **10**, 617; *J.*, 1918, 633A.

[24] *J.*, 1917, 1138.

[25] *Philippine J. Sci.*, 1917, A **12**, 49–110; *J.*, 1918, 97A.

A further section deals with attempts to press the freshly grated meal, but the results are not a success, even when the meal is heated with water previous to expression, as emulsions form which are difficult to separate. The press cake, however, is suitable for human consumption, and can be used in edible products.

The rancidity of the oil is considered in the light of tests for rancidity and content of free fatty acids, and the authors confirm the well-known observation that the magenta test is of no use as a test for the former change. They are of the opinion that the "oxidisability number" is largely a criterion of rancidity.

The rendering available of new sources of coconut oil is undoubtedly of considerable interest at the moment, and the experiments of these authors as directed to improvement of the product from the Philippines are of the greatest interest and value. In this connection the work of M. B. Smits[26] on the preparation of copra in Java may be noted, dealing with the yield of copra from nuts in different stages of ripeness.

There have lately been several attempts to patent processes for the preparation of coconut oil direct from the fresh meal, with the idea in view that the oil so obtained will be fit for edible purposes without further treatment.[27] The difficulty which always arises in these cases is that very stable emulsions of oil and water usually appear during the process, and without great care a high working loss results. In our experience the oil so obtained requires further refining to produce a "margarine" oil comparable with the product as usually manufactured (see above, H. C. Brill).

Olive Oil.—The stability of this oil on keeping is the subject of work by E. B. Holland, J. C. Reed, and J. P. Buckley,[28] the tests extending over a period of six years. The factors investigated were (1) air, (2) water, and (3) light, each being tried alone and in combination. Air alone destroys colour and produces slow rancidity and

[26] *Teysmannia*, 1916, **27**, 1495; *J.*, 1918, 33A.

[27] *See, e.g.*, G. C. Turner and C. H. Leighton, U.S. Pat. 1247597; *J.*, 1918, 34A.

[28] *J. Agric. Res.*, 1918, **13**, 353; *J.*, 1918, 474A.

decomposition of the unsaturated glycerides. Light has less effect in the production of rancidity. Together the effect is very marked and rapid. Moisture appears to produce slow hydrolysis. The exclusion of these three factors results in stability. It may be remarked that these conclusions need not apply only to olive oil, as they are known to be true for liquid vegetable oils in general.

Pentadesma Butyracea.—Several parcels of these kernels have appeared in England lately, and an analysis of a consignment has been published.[29] The fat, whilst usually light yellow and somewhat soft in character, appears to have possibilities, but the trees are rather sparsely scattered, and the kernels may be somewhat expensive to gather, and their value is also rather lessened by the uselessness of the cake for feeding purposes. The figures given are: m. pt. 33° C., saponification value 191·7, iodine value 42·8%. We have examined several samples of these fruits in which we find the oil content to vary from 35 to 53%, and the constants for the fat as follows: m. pt. 32°–38° C., saponification value 191–198, iodine value 35–46, refractive index (Zeiss) at 40° C. 43–47, and unsaponifiable matter 1·1–1·3%.

It is evident that there is considerable variation in the characteristics of the fat obtained from various consignments. The tree is known as the Sierra Leone tallow tree, and the fat as "Lamy" butter.

Piassava Oil.—A sample of this oil has been described by the Imperial Institute authorities (*loc. cit.*). It resembles patua oil in several respects, and is believed to be obtained from a species of *Raphia*. The figures given for it are: saponification value 192·7, iodine value 79·5%, titre 41·1° C.

Po-Yoak Oil.—This has also been examined at the Imperial Institute.[30] The nuts yield an oil having an odour something like that of tung oil, though apparently it does not polymerise in the same way, but thickens like linseed oil at 280° C. An iodine value of 156·9% places it among the drying oils, the properties of which it possesses.

Sejen (Unamo) Oil and Tacay Oil.—These oils, obtained from plants in Colombia, have been examined by A. L. Bacharach.[31] Both appear to be edible, and the former closely resembles olive oil. The following figures are given by the author.

	Sejen Oil.	Tacay Oil, extracted.
Yield of oil	..	53·3%
Sp. gr., 15°/4° . . .	0·9161	0·9220
Iodine value	73·5– 74·8	108·5
Saponification value . .	188·5–190·5	188·1

[29] *Bull. Imp. Inst.*, 1918, **16**, 35; *J.*, 1918, 594A.

[30] *Ibid.*

[31] *Analyst*, 1918, **43**, 289; *J.*, 1918, 553A.

Rhus Fats.—The fats have been separated from two varieties of *Rhus* (*R. laurina* and *R. diversiloba*) by J. B. McNair,[32] and these show marked differences, the former having a saponification value of 157·1, whilst that of the latter is 220·6. The fats appear to resemble Japan wax, which is the product of *Rhus vernicifera* and *Rhus succedanea*, and has a saponification value corresponding to that given by McNair for *Rhus diversiloba.*

Garcinia Tonkinensis.—F. Heim[33] has reported on Câydoc or Câygioc oil, obtained from the seeds of this plant, which is a native of Tonkin. It is there used as a burning oil, as it contains a pleasantly smelling ethereal oil. It would appear, however, to be of interest to the soap maker, as the fat is a mixture of glycerides and an oleo-resin, the latter constituent causing the soap to lather even with water hard from the presence of calcium sulphate.

Rice Polishings Oil.—According to F. Garelli[34] these polishings have usually been sold as a fertiliser or feeding stuff. They, however, contain 6·5% of oil available for expression. The oil must be obtained quickly, as otherwise it tends to become rancid rapidly on account of the porous character of the meal. The press cake contained nitrogen 2·73% and fat 8·68%.

SEED OILS.

Cucumber Seed Oil.—The wild cucumber is found in large quantities in British Columbia and California, and the seeds yield about 30–35% of oil. M. R. Daughters[35] has prepared specimens of the oil, both by extraction and expression. There is nothing very characteristic about the values obtained; the saponification value for the extracted oil is 193·4 and for the expressed oil 189·1, the corresponding iodine values being 116·5 and 117·0. The oil resembles olive oil in appearance and taste, the original green colour rapidly fading to a golden yellow.

Curcas Oil.—This oil, also known as pulza oil, and obtained from the fruits of *Jatropha curcas* or the physic nut tree, has been largely imported into France from Cape Verde and the Comoro Islands. Recently samples have been received from Madagascar.[36] The seeds contain 52% of oil in the kernels, and 31·6% in the whole fruit. So far it only finds an outlet for soap making, but it is considered that it might be used as a lubricant on account of its low acidity. Some samples examined by us confirm the yield of oil, and the general characteristics of the product. We have found the oil to have a saponification value of 182 and iodine value of 97%, the refractive index (Zeiss) at 40° C. being 55·7.

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[32] *Bot. Gaz.*, 1917, **64**, 330; *J.*, 1918, 430A.

[33] *Bull. Econom. de l'Indochine*, 1917, **20**, 135; *J.*, 1918, 63A.

[34] *Annali Chim. Appl.*, 1917, **8**, 109; *J.*, 1918, 187A.

[35] *J. Ind. Eng. Chem.*, 1918, **10**, 126; *J.*, 1918, 187A.

[36] *Rev. Agric. et Veterin. de Madagascar*, 1917, **2**, 37; 1917, **8**, 1303; *J.* 1918, 63A.

Fir Seed Oil.—This oil has been examined by J. Prescher,[37] who finds that the seeds give a yellow drying oil, the yield being about 33% of the dried seeds. It is characterised by a high iodine value, 155·8, and refractometer number (Zeiss) 78·2 at 25° C. The other figures are not noteworthy in any way except a slight Reichert-Meissl value of 1·2.

Pumpkin Seed Oil.—The pressure of circumstances in Roumania has caused attention to be turned to the utilisation of the seeds of a local form of pumpkin which is very rich in seeds. The seeds, after drying, yield 40–42% of green oil, which can be refined to give a good edible product. E. W. Albrecht,[38] in giving details of the manufacture, states that it is advisable to dry the seeds well before pressing.

Tomato Seed Oil.—A very interesting account of the use of tomato seed and skins is given by F. Rabak.[39] It appears that about 1500 tons of dry seeds become available annually, which yield on extraction 22% of oil. This oil is somewhat bitter and rancid, but is easily refined and deodorised by the usual processes, when a product, pale yellow in colour and of a pleasant nutty taste, is obtained. The oil has a saponification value of 188·6 and iodine value of 114·2. The solidifying point of the fatty acids is 20·5°–21·5° C., and the iodine value of the liquid fatty acids 130. These latter constitute 75·8% of the total acids present. The fatty acids consist chiefly of stearic, palmitic, oleic, and linolic acids, the proportions of the two latter being about equal. The oil is quite satisfactory as a salad and margarine oil, particularly if hydrogenated for the latter purpose. The meal is of good nutritive value, containing 37% of protein, though somewhat high in fibre (22%). The skins are usually mixed with this meal.

KERNEL OILS.

Apricot Kernel Oil.—The oils from the seeds of the Mongolian apricot (*Prunus armeniaca*) and also of the Chinese variety which is the same botanical species, have been examined by S. Ueno,[40] with the following results:

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[37] *Pharm. Zentralh.*, 1917, 58, 533; *J.*, 1918, 34A.

[38] *Z. angew Chem.*, 1918, 31, 132; *J.* 1918, 474A.

[39] *Bull.* No. 632, *Bureau of Plant Industry, U.S. Dept. of Agric.*, Nov. 30, 1917; *J.*, 1918, 70A.

	Mongolian.	Chinese.
Oil content in kernel	54 %	53%
Acid value	0·7	3·75
Saponification value	188·6	182·3
Iodine value	105·4	90·4

Though these two plants are botanically the same, it will be seen that the two oils are markedly different in their constants, probably due to difference in cultivation; in the case of the Mongolian specimen the figures are not very different from those published by the same author in 1913, but those for the Chinese specimens are decidedly different from the general run of these kernel oils.

Cherry Kernel Oil.—The oil obtained from the kernels of dried cherry stones, *Prunus cerasus*, has been examined by H. L. Maxwell,[41] who finds it to have a saponification equivalent of 276·8 and sp. gr. 0·922–0·925. The residue, as is to be expected, contains amygdalin.

DRYING OILS.

Linseed Oil.—A very interesting paper is contributed by G. E. Holden and L. G. Radcliffe,[42] on the oxidation of this oil. The experiments included determination of increase of weight on drying at different temperatures, and the diminution at higher temperatures is attributed to the more rapid formation of volatile substances. Oils having a low iodine value are the slower dryers, but apparently from the results obtained the saturated glycerides present have a decided influence on the rate of drying.

The volatile products obtained by drying at 100° C. gave reactions for unsaturated aldehydes, and also contained free fatty acids. The hardness of the oxidised oils seems to be dependent on the non-drying constituents of the oil.

Lumbang Oil.—R. H. Aguilar[43] has drawn attention to the value of lumbang oil as a substitute for linseed oil in paint media. Two varieties of the oil, *L. bato* and *L. banucalag*, the former derived from *Aleurites moluccana* and the latter from *A. trisperma*, have been carefully examined. Individually neither of these oils appears to approach linseed oil, particularly *L. banucalag*, but in combination in mixtures of 1 : 1 or 1 : 3 parts of *L. bato* to *L. banucalag* very satisfactory results were obtained in conjunction with red lead. Both the drying and the moisture-excluding properties were very nearly as good as those obtained in careful experiments with linseed oil.

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[40] *Kōgyō-Kwagaku-Zasshi*, 1918, **21**, 525; *J.*, 1918, 707A.

[41] *Chem. News*, 1918, **117**, 122; *J.*, 1918, 214A.

[42] *J. Soc. Dyers and Col.*, 1918, **34**, 138; *J.*, 1918, 429A.

[43] *Philippine J. Sci.*, 1917, **12 A**, 235; *J.*, 1918, 215A.

A similar anomalous result has been noted by S. Rideal and L. H. D Acland[44] with regard to mixtures of the oils obtained from varieties of *Ceara* and *Funtumia.*

Para Rubber Seed Oil.—Interesting details of the possibilities of this oil are furnished by F. G. Spring and F. W. F. Day.[45] A yield of 300 lb. per acre is now obtained and the seed can be stored quite satisfactorily after sun-drying. The authors give the following figures for some samples examined by them. Sp. gr. (15°/15° C.) 0·925–0·930, saponification value 188·5–192·1, and iodine value 128·3–143·3.

It is certain that an effort should be made to utilise this oil, which is now available in considerable quantities, as, though less valuable than linseed oil, especially as regards drying power, yet in the serious shortage of this oil, attempts might well be made to utilise it in several directions. It is interesting to note that attention has again been drawn to the fact that para rubber seed cake forms a satisfactory feeding stuff.

Oiticica Oil.—The seeds of *Conepia grandifolia*, belonging to the large order of *Rosaceæ*, contain kernels which give a yield of 62% of a curious drying oil with some remarkable properties. These seeds have been coming to this country in small quantities, and have been examined by E. R. Bolton and C. Revis.[46] The oil was very difficult to work with, as, when liquid, it oxidises with great rapidity. It resembles in some ways tung oil, and forms a gelatinous mass when heated in an atmosphere of carbon dioxide to 300° C., but a vigorous evolution of gas takes place at the moment of setting. The iodine value of the oil is 179·5, one of the highest values yet recorded.

Sanga-Sanga Oil.—Another drying oil has been recently described by Pieraerts[47]; it is obtained from the nuts of a variety of *Ricinodendron* found in French Congo and other parts of West Equatorial Africa. The nuts, which are about the size of hazel nuts, yield 28% of kernel containing 55% of oil. The iodine value is not given, but the oil, on shaking with a saturated solution of iodine in chloroform, sets to a gelatinous mass. The oil dries more rapidly than linseed oil and can be used for waterproofing purposes. It shows a marked distinction from the last described oil (oiticica) by having a comparatively sharp melting point, viz. 32·3—34·5° C., the latter being very indefinite in this respect.

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[44] *Analyst*, 1913, **38**, 259; *J.*, 1913, 704.

[45] *Agric. Bull, F.M.S.*, 1918, **6**, 231; *J.*, 1918, 381A.

[46] *Analyst*, 1918, **43**, 251; *J.*, 1918, 430A.

[47] *Ann. du Musée Colon. de Marseille*, 1917, **5**, 27; *J.*, 1918, 430A.

Fish Liver Oils.

M. Tsujimoto[48] has continued his work on various liver oils, and in addition to those hitherto described, has now published figures for those obtained from globe fish and angler fish (*Spheroides porphyreus* and *Lophiomus setigerus*). Both these deposit "stearine" on standing and give a similar coloration with sulphuric acid. It may be noted that they belong to the class possessing only a small percentage of unsaponifiable matter, and further that this unsaponifiable matter contains no trace of "squalene." In distinction to these are the same author's results with three samples of the oil of the basking shark (*Cetorhinus maximus*),[49] which contained 42–56% of unsaponifiable matter in which "squalene" was identified. One, however, contained 10% of a saturated hydrocarbon, probably $C_{18}H_{38}$, as well. This is an interesting point, as it seems to give some little evidence that these hydrocarbons are quite possibly transition products and in a state of flux in the liver. This particular sample of liver oil had an iodine value of 178·3 and unsaponifiable matter 41·9%. The author describes the preparation of derivatives of "squalene" by which it can be easily identified. It may be of interest to collect this author's results noted last year (*Ann. Reports*, ii. 311) with these later ones.

	Saponification value.	Iodine value.	Refractive index, 20°C.	Unsaponifiable matter. Per cent.	Insol. bromides from fatty acids. Per cent.
Globe fish	182·2	159·8	1·4785	1·47	46·65
Angler fish	188·6	154·1	1·4790	1·00	44·13
Basking shark	102·45	178·3	1·4773	41·92	..
Shark (Moroccan)[50]	22·5	358	..	89·1	..
Calamary oil	189·6	177	1·4806	1·14	57·5
Sun fish	180·2	151·8	1·4786	3·20	43·5
Common ray	182·7	183·7	1·4825	3·15	60·2

In another communication[51] the question of the classification of shark liver oils has been further considered by the same author, and he divides them into two groups according as the specific gravity at 15°/4° C. falls below or above 0·9000. The former division, derived from members of the family *Squalidæ*, are all rich in "squalene," whilst the latter group, with two exceptions, are free from it. The oils of the first group are naturally distinguished by high iodine values and low saponification values.

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[48] *Kōgyō-Kwagaku-Zasshi*, **1917, 20,** 709; *J.*, **1918, 63A.**

[49] *J. Ind. Eng. Chem.*, **1917, 9,** 1098; *J.*, **1918, 98A.**

[50] Chapman, *J.*, **1917, 392.**

[51] *Kōgyō-Kwagaku-Zasshi*. **1917, 20,** 953, 1069; *J.*, **1918, 312A.**

A. C. Chapman[52] has examined two samples of dog fish liver oil after separation of the "stearine." Both these agree with the classification given above as regards saponification and iodine values. From the results obtained, this author is of the opinion that the proportion of unsaponifiable matter depends on the age and condition of the fish.

The same author[53] has also published further details with regard to the constitution of spinacene. A careful investigation of the changes taking place during distillation over sodium has led to more suitable methods being devised, and the formula $C_{29}H_{48}$ is now given to the substance.

Fish Oils from Fresh Water Fish.—M. Tsujimoto,[54] in addition to his studies on the liver oils of marine animals, has also investigated the oils derived from certain fresh water fish, notably carp, loach, and trout. The oils are not markedly different from those of sea fish, beyond yielding a lower percentage (22%–28%) of insoluble bromides from the fatty acids, except in the case of one variety of trout, in which the figure, 46·3%, is as high as those of sea fish. They appear to contain a lower percentage of bromine.

Fish Oils.—W. Fahrion[55] has confirmed the presence of jecoric acid, $C_{18}H_{30}O_2$, in sardine oil in addition to the clupanodonic acid of Tsujimoto. The author also maintains that the acid called by him asellinic acid, $C_{17}H_{32}O_2$, and found in liver oils, is actually an individual acid and not a mixture. The interest in this acid lies in the fact that, if an actual entity, it is one of the few fatty acids found naturally which contain an odd number of carbon atoms.

VARIOUS SUBSTANCES.

Gossypol.—The attention being paid again to cotton oil makes two investigations on this toxic principle of the seed of interest. The work of W. A. Withers and F. E. Carruth[56] records the results of a number of feeding experiments. It appears that the meal, as it usually results from pressing, is less toxic than the raw meal on account of the oxida tion of the gossypol. As extracted meal would probably be subjected to a higher temperature than this during driving off of the solvent, possibly the same results would have been found with the extracted meal. It is highly desirable that such tests should be made with extracted meals, as the supposed ill-effects with soya extracted meal need a good deal of confirmation.

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[52] *Analyst*, 1918, **43**, 156; *J.*, 1918, 312A.

[53] *Chem. Soc. Trans.*, 1918, **113**, 408; *J.*, 1918, 381A.

[54] *Kōgyō-Kwagaku-Zasshi*, 1917, **20**, 711; *J.*, 1918, 63A.

[55] *Chem. Umschau*, 1917, 57; *J.*, 1918, 630A.

[56] *J. Agric. Res.*, 1918, **12**, 83; *J.*, 1918, 164A.

One of the above authors (Carruth), in a further paper,[57] deals with some of the changes which take place in this substance. Apparently by cold pressing, the oil can be obtained free from gossypol, but this does not apply to the commercial " cold " pressing in which a good deal of heating of the meal occurs. In " hot " pressing, oxidation takes place, and the altered gossypol is largely left in the cake. For this reason this author infers that the " hot " pressed oil should be more economical in refining.

Colouring Matters.—In this connection reference may be made to the work of A. H. Gill[58] on the presence of carotin in oils, &c. Besides its presence in palm oil, Gill has now identified it in maize, pumpkin, mustard, black sesamé, butter fat, tallow, &c., but has not found it in rape, white sunflower, safflower, or turmeric.

Vitamines.—The subject of vitamines is not directly connected with the edible oil and fat industry, but so much attention has been drawn to the lack of these substances in vegetable fats used in the production of edible products that a paper by W. Ramsden[59] will be of interest to those concerned. It is argued that these substances are to be found in natural hard fats of animal origin such as butter, oleo oil, &c., and are therefore necessary. The absence is not to be wondered at in the refined vegetable fats which have been subjected to very high temperatures in refining—such temperatures as are not experienced by the animal products. The idea has naturally been taken up as a useful advertisement by some of those who employ the animal fats, but the undesirability of vegetable fats on account of the absence of vitamines seems a little far-fetched, and there is no need for alarm. (See also under Foods, p. 409.)

INDIAN SCIENCE CONGRESS.

In the reports of the Congress held at Lahore in January 1918,[60] there are several papers dealing with vegetable oils and fats. These can only be briefly noted under their titles.

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[57] *J. Amer. Chem. Soc.*, 1918, **40**, 647; *J.*, 1918, 319A.

[58] *J. Ind. Eng. Chem.*, 1918, **10**, 612; *J.*, 1918, 633A.

[59] *J.*, 1918, 53T.

[60] *J.*, 1918, 193R.

(1) "The Coconut," by N. Kunjan Pillai, chiefly dealing with the cultivation and insect pests.
(2) "The Hydrolysis of certain Indian oils by Castor Lipase," by K. G. Latwala. The oils dealt with are cotton, arachis, and hongay.
(3) "Safflower Oil," by H. H. Mann and N. V. Kanitkar.
(4) "Safflower Oil, Chemical studies and its Germination," by V. A. Tamhane.

ANALYTICAL METHODS.

The methods of analysis published during the last twelve months present no striking features, though several papers deal with points which are worthy of consideration. Possibly the efforts of the Ministry of Edible Oils and Fats directed towards the standardisation of methods employed in the analysis of oils and fats and the unification of methods of sampling and of dealing with samples prior to analysis, will prove of the greatest interest to those employed in such work. The results of their efforts will probably soon be in the hands of chemists. The question of standardisation is a decidedly vexed one, as, though such standardisation tends to minimise differences and to co-ordinate results, it also fetters very much the free action of the chemist in improving and advancing analytical science. Methods laid down in such a manner should be revised at frequent intervals in order to guard against the perpetuation of error, and, to make such revision of value, there should be continual investigation carried on in connection with it.

Determination of Oil in Seeds.—W. B. Gray[61] draws attention to the greater value of the continuous percolation type of extractor, such as that of Kreussler, over the Soxhlet type for estimating the oil contained in oil seeds. It is an unfortunate fact that the Soxhlet type still continues in use for this purpose, as it is not nearly so satisfactory in general as the other form of extractor, or those of similar action, and the new Journal may be congratulated on drawing attention to the fact in one of its earliest papers. There are times in which the Soxhlet has its advantages, notably when dealing with pulp containing much tough fibre, as this cannot be ground finely, and is not so conveniently dealt with by continuous percolation.

Butter Fat.—The method described by E. B. Holland and J. P. Buckley[62] for the determination of fatty acids in butter fat, can scarcely

[61] *J. S. African Assoc. Anal. Chem.*, 1918, 1, 5; *J.*, 1918, 430A.
[62] *J. Agric. Res.*, 1918, 12, 719; *J.*, 1918, 346A.

be looked upon as an analytical method, as the esterification of fats and subsequent fractionation of the esters is a process requiring considerable time and care for its successful performance. The method has been brought into prominence lately, and was referred to in the Reports, 1917 (p. 313). The fractions collected after separation of alcohol and ether were 125°–180°, 180°–225°, 225°–270°, 270°–300°, 300°–325°, and 325°–365° C. Each fraction is supposed to contain the esters of three acids, the proportions of which are determined from the saponification and iodine values. The results are very interesting, but it must be borne in mind that the experimental error must be high. The results obtained are given below in comparison with some results recorded by other observers, and noted in last year's Report. The figures given are percentages of fatty acids.

Acids.	Holland and Buckley.	Crowther and Hynd.
Butyric	3·15	4·27
Caproic	1·36	1·64
Caprylic	0·97	1·16
Capric	1·83	1·19
Lauric	6·89	5·01
Myristic	22·62	16·43
Palmitic	19·23	14·83
Stearic	11·38	3·40
Oleic	27·34	44·42
Dihydroxystearic acid	..	0·38

The glycerides of butter fat have also been investigated by C. Amberger,[63] but the work is directed to the constitution of these glycerides rather than to the quantitative yield of fatty acids, which forms the basis of the work of Holland and Buckley. By fractional crystallisation of a hydrogenated derivative of the fat, he has apparently established the fact that much of the olein present is not in the form of triolein but as mixed glyceride, and the existence of butyro-diolein and butyro-palmito-olein is postulated. In general it would appear that mixed triglycerides are rather the rule in butter fat.

Castor Oil.—C. Frabot[64] has made a further investigation into the use of petroleum spirit as a solvent for castor oil in the detection of foreign oils which may be mixed with it, particularly when the oil is to be used for lubricating purposes. It appears that the solubility of castor oil depends very much on the boiling point of the spirit used, the solvent power increasing with the rise in b. pt.; thus, the fraction boiling at 33·2° C. dissolves 6·5 grms. of castor oil under the author's conditions, whilst a fraction boiling at 184° C. dissolves 25·3 grms. The increase in volume of the spirit, owing to the solution of the oil, does not increase at quite the same rate. The author suggests the use of spirit boiling between 35° and 65° C., which dissolves 8·85 grms. and shows an increase in value of 11·5 c.c.

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[63] *Z. Unters. Nahr. Genussm.*, 1918, 35, 313; *J.*, 1918, 558A.

[64] *Ann. Chim. Anal.*, 1918, 23, 7; *J.*, 1918, 98A.

In a further communication[65] the author answers the objection that the solvent power of petroleum spirit varies, but maintains that it is sufficiently accurate if a control with a known mixture be done at the same time. The criticism of this method emanated from N. Chercheffsky,[66] who proposes in opposition the determination of the critical temperature of the oil in ethyl alcohol (sp. gr. 0·8481 at 15° C.). Ten drops of oil and 40 drops of the alcohol are placed in a tube 10 cm. long and 6–8 mm. in diameter, which is then sealed off. The tube is heated till the dividing meniscus becomes flat, when the oil and alcohol are mixed without removing the tube from the bath, which is then allowed to cool. The temperature of permanent turbidity is noted. Castor oil gives a figure of 66°–67° C., which is the lowest of oils likely to be used for adulteration, as 2% of any of these such as rape, arachis, cotton seed, linseed, or fish oil will raise this temperature to 69°–71° C.

Sulphonated Oils.—G. W. Schultz[67] has carried out a number of analyses, using a modification of Hart's method,[68] and has compared the results with those obtained by the official methods of the American Leather Chemists Association Committee. The figures obtained for neutral fat by the author are much higher than those obtained by the Committee's method, but the results are considered to be accurate and reliable. The method appears to be simple and the principles involved sound.

Iodine Value.—C. Kelber and H. Rheinheimer[69] have carried out a series of comparative tests with the Wijs and Hübl methods and the bromide bromate method of Gabel.[70] They found that this latter method will give concordant results with the standard processes in case of low iodine values, but the absorption of iodine is not complete in the case of fats with high iodine values. We have also investigated this method as described by Vaubel,[71] and arrived at very similar conclusions.

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[65] *Ann. Chim. Anal.*, 1918, **23**, 120; *J.*, 1918, 474A.

[66] *Ibid.*, **23**, 75; *J.*, 1918, 273A.

[67] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 190; *J.*, 1918, 431A.

[68] *J.*, 1917, 1139.

[69] *Arch. Pharm.*, 1917, **255**, 417; *J.*, 1918, 34A.

[70] *Ibid.*, 1912, **250**, 72.

[71] *Z. angew. Chem.*, 1910, **23**, 2077.

Sesamé Oil Reaction.—F. Weehuizen,[72] arguing from the work of other investigators as to the causative substance in the reagent usually employed in the Baudouin test, has come to the conclusion that the use of furfural in the test is incorrect, and maintains that sugar should be used. He suggests the use of either sucrose or lævulose shaken with 3–5 c.c. of an alcoholic solution of hydrochloric acid, this being mixed with an equal volume of the oil and shaken for one minute. While there is no doubt that the substance formed from the sugar is a hydroxymethylfurfural, it cannot be denied that furfural itself in alcoholic solution gives excellent results when testing for sesamé oil, though it is evident that substituted derivatives of furfural act in a similar manner.

The Valenta Test.—This useful test has always suffered in its practical application from the diversity of results obtained by different observers. This undoubtedly arises from the sensitiveness of the test to slight variations in the strength of the acetic acid used. For this reason P. J. Fryer and F. E. Weston [73] have suggested a new reagent and a method of standardisation which bids fair to remedy these objections very largely. They use as the solvent a mixture of equal volumes of 90–92% alcohol and amyl alcohol, and standardise this solution with pure almond oil so as to give a turbidity figure of 70° C. This solvent brings most oils and fats into a satisfactory range of temperature. These authors have also carefully investigated the effect of free fatty acids on the values obtained, and the necessary corrections to be made have been worked out for the various classes of oils and fats; for instance, each 1% of acidity as oleic acid for marine oils gives a depression of 1·95°, of drying oils 2·05°, semi-drying oils 2·03°, and non-drying oils 2·07°, and so on. This point is of importance, and has been too little considered in the application of the Valenta test. The test has also been applied with success to the differentiation of animal and vegetable waxes, and to the admixture of one with the other. It is to be hoped that more attention will be paid to this new method by other workers.

A. E. Parkes [74] has also dealt with this test, and has attempted to obviate the difficulties of the acetic acid by using a mixture of 88–89% glacial acetic acid with 10% of propionic acid and 1–2% of water. This reagent remains liquid at 0° C. and is standardised against pure butter fat. This latter substance, however, is scarcely a satisfactory one, as butters give rather wide variations for the turbidity temperatures.

[72] *Pharm. Weekblad*, 1918, **55**, 77; *J.*, 1918, **249A**.

[73] *Analyst*, 1918, **43**, 3; *J.*, 1918, **64A**.

[74] *Analyst*, 1918, **43**, 82; *J.*, 1918, **214A**.

Determination of Resin in Soap.—V. Fortini takes exception to the usual Twitchell method of determining resin acids in soaps, on the ground that pure soaps show an apparent content of resin by that method. He describes a method[75] by which this objection is overcome. Two grms. of the suspected acids is treated with 50 c.c. of petroleum spirit in a separating funnel. Ten c.c. of nitric acid prepared by mixing 1 pt. of fuming acid (sp. gr. 1·52) and 3 pts. of acid sp. gr. 1·48, and treated with a little urea to destroy any nitrous acid, is gradually added with shaking. After standing, the acid layer is drawn off, and the ether layer again shaken with 5 c.c. of the nitric acid, which is run off. The ether is then washed with ordinary nitric acid and with water, filtered, and the ethereal filtrate evaporated to dryness. This ether is supposed to contain only the fatty acids, as according to Fortini, the nitrated resin acids are insoluble in petroleum ether. The method appears to be quicker and less cumbersome than the ordinary esterification method, though whether it be quite as accurate can only be determined by careful experiment.

Acid Oils.—The present methods for the manufacture and sale of acid oils and soap stocks have led to considerable divergence in many cases in the composition arrived at by different analysts. As many of these acid oils are derived from coconut and palm kernel oils, it is evident that the moisture cannot be estimated in the water oven. In order to standardise the process E. R. Bolton and C. Revis[76] have devised a method of distributing the acid oil on a long pleated strip of filter paper, which is subsequently dried in weighing bottles in the vacuum desiccator. The method, though a little slow, furnishes reliable and concordant results. They also describe in the same paper a quick and easy method of determining the total fatty matter in soap stocks, using a special flask for the purpose. It must be remembered that most of the divergence in the results obtained is often due to the very great difficulties experienced in drawing reliable and representative samples from the barrels containing the acid oil or soap stock, as separation, especially in soap stock, takes place remarkably easily, and the ordinary "trier" does not withdraw a true section of the contents of the barrels.

Soaps and Fatty Acids.—P. J. Fryer[77] has drawn attention to the use of the Polenske method in the analysis of soaps and fatty acids which are derived from coconut and palm kernel oils. The process is carried out in the usual manner as with the whole oils. The author finds a figure of 17·3% for the insoluble volatile fatty acids of coconut

[75] *Annali Chim. Appl.*, 1918, **9**, 102; *J.*, 1918, 381A.
[76] *Analyst*, 1918, **43**, 158; *J.*, 1918, 312A.
[77] *J.*, 1918, 262T.

oil and 10·5% for those of palm kernel oil. It may not be out of place to draw attention in this connection to a point often overlooked in the preparation of the fatty acids of soap stock, viz. that in the case of coconut and palm kernel soaps, volatile fatty acids are present and may be partially lost if precautions be not taken.

Fatty Acids in Soaps.—The difficulties which arise from oxidation and volatility in these estimations have led E. Bosshard and F. Comte [78] to attempt to isolate and weigh them as lead salts. The method appears, however, to be rather cumbersome and to need care, and as it is necessary to determine also the mean molecular weight in a mixture in order to ascertain what correction must be made for the weight of lead, the method will hardly be rapid enough for works practice.

Calcium Soaps.—The effect of various solvents on these soaps has been studied by E. Salm and S. Prager [79] with interesting results. Of the solvents tried, acetone and ether alone did not cause the soap to swell and gelatinise, and as, in general, these soaps (castor excepted) are not soluble except with difficulty in acetone, whilst ether has a distinct solvent effect, the former solvent is to be preferred in separating neutral fat from such soaps. Difficulty arises with petroleum spirit, as this causes swelling of the soap.

Colour in Butter and Margarine.—A scheme for the identification of colours used for this purpose is given by H. A. Lubs.[80] The methods follow to a certain extent the usual processes, but the scheme is more complete than usual. It is rather vitiated by the apparent necessity for the use of 1–2 lb. of fat at one stage of the procedure, as the unfortunate analyst is not always in possession of these wholesale quantities on which to do a complete analysis. This examination on the large scale, however, is directed to the identification of the various azo dyes employed.

Standard Methods for sampling and analysing oils and fats other than those of the coconut, butter, and linseed groups have been worked out by a Committee of the American Chemical Society.[81] The methods proposed are tentative and unfortunately suffer from the failing usually found in methods settled by Committees, viz. that they are quite impossible for the ordinary chemist to adopt. For instance, not less than 3 lb. of sample is to be accepted, though the ordinary chemist has usually to be contented with as many ounces. To determine moisture a specially designed vacuum oven is required in which the temperature can be maintained 15°–20° C. above the boiling-point of water at the pressure used, which must be less than 100 mm. of mercury. For the titer test the use of a 25% solution of caustic soda in glycerin is substituted for the usual alcoholic saponification. It is satisfactory to note that the Committee advises the use of petroleum spirit in determining unsaponifiable matter rather than ethyl ether.

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[78] *Helv. Chim. Acta,* 1918, **1,** 251; *J.,* 1918, 707A.

[79] *Chem.-Zeit,* 1918, **42,** 463; *J.,* 1918, 707A.

[80] *J. Ind. Eng. Chem.,* 1918, **10,** 436; *J.* 1918, 482A.

[81] *J. Amer. Leather Chem. Assoc.,* 1918, **13,** 14; *J.,* 1918, 157A.

Rancidity.—R. H. Kerr[82] remarks on the tests for rancidity that Kreis' test[83] with resorcinol and hydrochloric acid is very sensitive, and will give indications before rancidity is detected by organoleptic tests. There is no doubt but that this test is a remarkably sensitive one for aldehydes, as is shown by the small traces of invert sugar that can be detected by it. Kerr has also investigated the "oxidisability figure," and is of the opinion that it is nothing like so delicate, and that a low figure cannot be taken as evidence of the absence of rancidity (see also p. 270).

Relationship between Chemical Constitution and Refractive Index.—It was pointed out in last year's Reports that work in this direction was very necessary and likely to lead to advantageous results. C. Cheneveau,[84] assuming that a liquid fat may be taken to consist of a solution of solid glycerides in liquid glycerides, maintains that the law of solutions holds good, and that the refractive index of the oil may be calculated from the percentage proportions of the two series of glycerides and of their refractive indices. Further assuming that the iodine value is a true measure of the liquid glycerides, a relationship between the iodine value and refractive index is arrived at.

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[82] *J. Ind. Eng. Chem.*, 1918, **10**, 471; *J.*, 1918, 475A.

[83] *J.*, 1904, 1001.

[84] *Comptes rend.*, 1917, **165**, 1060; *J.*, 1918, 64A.

PAINTS, PIGMENTS, VARNISHES, AND RESINS.

By Capt. L. M. Nash,
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The progress in these industries during the year does not appear to have been very striking, doubtless due in some measure to the attention of many chemists having been occupied with other matters, temporarily of more importance. Owing to the restriction of imports and consequent cessation or reduction of supplies of certain materials, the question of substitutes becomes more and more important, and much research is required at a time when opportunities of carrying it out are limited.

The cutting down of the supply of linseed oil to paint and varnish manufacturers, owing to the requirement of glycerin for explosives, has resulted in the preparation of a drying oil from the fatty acids of this oil. It is stated that this is a satisfactory substitute, but time alone can prove its lasting properties.

The Properties of Drying Oils.

A further addition to the literature dealing with the oxidation of linseed oil is made by G. E. Holden and L. G. Radcliffe.[1] These authors introduced into a series of wash-bottles pieces of specially prepared cotton cloth impregnated with linseed oil. When a slow current of air was drawn through, it was found that the oil in the first bottle dried more rapidly than that in the second, whilst the second was more rapid than the third, and so on. After 450–500 hours, however, it was found—as might be expected—that the samples showed equal increments in weight (17–18 %). The bottles were then heated to 100° C., when the original gain was reduced to one of 1·0–3·5 %. Using smaller amounts of oil, spread on roughened glass plates and exposed to definite temperatures, the velocity of drying increased with the temperature, but the maximum increase and the influence of any driers present varied inversely with the temperature. At 34° C. the oil gained 17–18 %, at 100° C. 7·8 %, and at 150° C. no increase took place, probably owing to accelerated formation and evolution of volatile products.

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[1] *J. Soc. Dyers and Col.*, 1918, 34, 138–146; *J.*, 1918, 429A.

Linoleate and resinate of the same metal, containing the same proportion of that metal, showed an equal drying capacity, but manganese had six times the efficiency of lead as a drier. Turpentine only slightly increased the drying rate of linseed oil. Various results are given which indicate that the saturated glycerides have an important influence on the rate of drying of the oils, and the ultimate decomposition of a film of oil appears to be due to the decomposition and emanation of the non-drying substances in the film. Under the influence of ultra-violet rays linseed oil itself dries as rapidly as the oil containing driers.

Several oils possessing drying properties are described by various authors. These, although of general interest, are not likely to be used in the near future; for the present shortage of linseed oil is probably due more to the shortage of freight and large Government requirements than to any shortage of linseed oil itself.

Lumbang oils are described by R. H. Aguilar,[2] who states that the Bato variety had a specific gravity at 15° C. of 0·9252 and iodine value 150·36, the corresponding figures for the Banucalag variety being 0·9368 and 145·25. With the fresh oils the former increased 11·03 % in weight in four days in a drying test, and the latter 8·92 %. The latter oil by itself is not a satisfactory paint medium, although when mixed with the former in the proportion 1 : 1 to 3 parts it yields a rapid drying and satisfactory paint.

Oiticica oil has been examined by E. R. Bolton and C. Revis.[3] Brazilian seeds yielded 62 % of oil sp. gr. at 15·5°/15·5° C. 0·9694 and iodine value 179·5. Heated to 250°–270° C. in an atmosphere of carbon dioxide no solidification took place, whereas tung oil became solid under the same conditions. At 300° C. the oil polymerised, giving a stiff, transparent jelly. A thin film of the oil heated at 100° C. gained 4 % in weight (tung oil 2–3 %). The authors state that the oil will probably be suitable for the manufacture of linoleum as well as for varnish.

Sanga-sanga oil, described by Pieraerts,[4] is obtained from the nuts of *Ricinodendron africanum*, the kernels of which contained 55·29 % of the oil, sp. gr. 15°/15° C. 0·9345. It is stated to dry more rapidly than linseed oil and to be suitable for waterproofing, etc.

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[2] *Philippine J. Sci.*, 1917, **12A**, 235–243; *J.*, 1918, 215A.

[3] *Analyst*, 1918, **43**, 251–254; *J.*, 1918, 430A.

[4] *Ann. du Musée colon. de Marseille*, 1917, **5**, 27–37; *Bull. Agric. Intell.*, 1918, **9**, 456; *J.*, 1918, 430A.

J. Zellner[5] states that the oil from the elder seeds (*Sambucus racemosa*), (sp. gr. at 15° C. 0·934, iodine value (Hübl) 162·0), resembles linseed oil in its drying properties and other characteristics.

Para rubber seed from Malay yields 29 % of oil, or 51 % from the kernels (F. G. Spring and F. W. F. Day[6]), sp. gr. 15/15° C. 0·925–0·930, iodine value 128·3–143·3. The oil is stated to possess rather less drying power than linseed oil.

Po-yoak oil[7] has an odour resembling that of tung oil. Sp. gr. 15/15° C. 0·963, iodine value 156·9. The skin formed on drying is rather rough and not transparent. It is stated that the oil could be used in paints and varnishes, and that it thickens like linseed oil on heating at 280° C.

That further work is being carried out in the direction of preparing drying oils from mineral oils is evidenced by the patents granted to W. Dyer[8] and F. C. Thiele.[9] In the former, (*a*) 10–20 parts of non-drying mineral oil freed from gasolene and kerosene, and one part of alcohol, are boiled for a sufficient length of time to convert the mineral oil into a drying oil; (*b*) 9–19 volumes of mineral oil having a gravity about that of kerosene is boiled with one volume of alcohol for about half an hour. This preparation is claimed to have "drying properties," to be capable of hastening the drying of paints containing drying oils, and to possess a heavier "body" than kerosene, gasolene, or turpentine. In the latter patent, kerosene, containing cyclo-paraffins, is treated with a halogen (chlorine), acidulated, and the mixture treated with a metal.

A further patent granted to W. E. Dyer[10] describes the preparation of a drying oil from a non-drying or semi-drying fatty oil by admixture with alcohol and boiling.

The treatment of linseed oil fatty acids is described in a patent granted to J. Barry.[11] The fatty acids are stated to be rendered readily oxidisable, and thus suitable for the manufacture of linoleum and paints, by subjecting them to the action of superheated steam, preferably after heating in a steam-jacketed pan. The superheated steam decomposes any metallic compounds present, expels deleterious substances, and acts as an oxidation catalyst.

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[5] *Monatsh Chem.*, 1918, **39**, 87–94; *J.*, 1918, 519A.

[6] *Agric. Bull. Fed. Malay States*, 1918, **6**, 231–244; *J.*, 1918, 381A.

[7] *Bull. Imp. Inst.*, 1918, **16**, 34–40; *J.*, 1918, 594A.

[8] U.S. Pats. 1256535 and 1256537; *J.*, 1918, 251A.

[9] U.S. Pat. 1254866; *J.*, 1918, 188A.

[10] U.S. Pat. 1256536; *J.*, 1918, 251A.

[11] Eng. Pat. 118228; *J.*, 1918, 595A.

Properties of Varnishes.

The colour of oil varnishes may be satisfactorily matched, according to F. A. Wertz,[12] by solutions of potassium bichromate in strong sulphuric acid. The liquids are compared by transmitted light in tubes of definite diameter. It is stated that heating the solution to prevent decomposition of chromic anhydride does not appear to have any appreciable effect on the colour comparison.

The hardness and viscosity of varnishes are dealt with by R. P. L. Britten,[13] who states that the varnish maker's practical "thumb-nail test" is inadequate. The mechanical hardness testers of Laurie and Baly, Johns and Clemens, measure toughness rather than hardness. The author's method of determining true hardness is based on the principle of the hardness of minerals scale, scratched points of various crystals of known relative hardness being used. A method embodying the use of gelatin points of differing water content and registering results obtained in degrees of water is also suggested. In regard to viscosity those types of instruments are recommended in which force as against time is the factor determined. The author has elaborated a type of viscometer having for its principle the determination of the time taken for a glass or metal ball suspended on one arm of a balance of high moment of inertia to fall a definite distance through the liquid. The times taken under similar conditions in air and in water serve for the standardisation of the instrument ("retardation in water") Viscosity is calculated as time divided by the retardation for water. As equilibrium is adjusted after immersion of the ball, a correction is made for specific gravity.

To protect gums from the air during the process of melting, O. C. Griem[14] patents a method for covering them with water and heating till the particles soften and flow together, when the water is poured off, and the heating continued until the gums are completely melted.

R. Weeber[15] describes the preparation of varnish from a semi-drying oil—such as train oil—by treatment in a comparatively cold state with a lye to saponify the free fatty acids, and after the removal of the soap thus formed, polymerising the oil to a varnish with the aid of driers. The use of sulphur in varnish is suggested by O. Brocking,[16] who heats together copal resin, fatty oil, and sulphur to form a homogeneous mixture and then raises the temperature to form a varnish.

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[12] *J. Ind. Eng. Chem.*, 1918, **10**, 475; *J.*, 1918, 476A.

[13] *Oil and Colour Chem. Assoc.*, Sept. 1918; *J.*, 1918, 594A.

[14] U.S. Pat. 1265326; *J.*, 1918, 476A.

[15] U.S. Pat. 1257562; *J.*, 1918, 251A.

J. Fluss and J. Tanne,[17] dealing with resins of the olibanum series, subject them to dry distillation to remove ethereal oils. The residue is extracted with low-boiling solvents, *e.g.*, dichlorethylene, whereby only the resinous substances are removed and injurious impurities remain. In this way it is claimed that a hard, quick-drying varnish of a high degree of gloss, transparency, and resistance to weather and water, is obtained. S. Langguth [18] patents a method for obtaining waterproof coatings by extracting with benzol or alcohol naphthol pitch, *i.e.* the condensation product formed in the preparation of α- and β-naphthol, whereby a resin is obtained which is insoluble in soda. S. Satow [19] produces a lacquer by "glutinising" vegetable proteins with a phenol to form a liquid, adhesive, glue-like mass, and treating it with an active methylene compound, *e.g.* formaldehyde, controlling the consistency with benzene. The lacquer is used for coating bricks, cement, tiles, or similar substances shaped without heat.

In examining varnishes to discover the nature of the drier used, cobalt compounds should be sought for, as they are occasionally employed. E. G. Jones [20] states that small quantities (0·01–0·1%) may rapidly be determined colorimetrically by means of a solution of α-nitroso-β-naphthol, the effect of many other metals being eliminated by the addition of ammoniacal ammonium citrate solution. The ash from the varnish is treated with strong hydrochloric acid, followed by *aqua regia*, and later by hydrochloric acid to remove the nitric acid, and then evaporated to dryness. The aqueous solution slightly acidified with hydrochloric acid is treated with ammonium citrate solution, and after addition of the reagent the colour is compared with that given by standard cobalt solutions under the same conditions. Copper, nickel, and manganese should first be removed by suitable means described in the paper.

The examination of oil varnishes is the subject of a paper by H. Smit-Addens.[21] Volatile thinners are estimated by steam distillation in a current of carbon dioxide, and the distillate is transferred to a burette containing 10 c.c. of water, the aqueous layer being examined for smell and acid reaction. The sp. gr. of the distillate can be determined in the case of turpentine by introducing a drop into alcohol of about 70% strength (sp. gr. 0·87 at 15° C.), adding more alcohol and water to obtain the correct sp. gr. For petroleum spirit a pyknometer is used. A second drop of the distillate serves for the determination of the refractive index. The residue from the steam distillation is freed from the bulk of the water, saponified, and extracted with petroleum ether in the usual way, the extract being weighed as copal resin. The soaps of the softer resins are not so easily hydrolysed, and are estimated along with rosin acids. If dammar is suspected, the soap is further extracted with ether. Copal is separated by chloroform or carbon tetrachloride. The extracted soap residue is examined for metals after acidification with dilute nitric acid and extraction with petroleum ether. The extract containing rosin acids and fatty acids is examined qualitatively by the Storch-Morawsky test and quantitatively by the Twitchell method. The hydroxy-fatty acids clinging to the walls of the separating funnel are dissolved in a mixture of equal parts of alcohol and carbon tetrachloride and calculated to oleic acid.

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[16] U.S. Pat. 1262302; *J.*, 1918, 340A.

[17] Ger. Pat. 302852; *J.*, 1918, 340A.

[18] Ger. Pat. 302741; *J.*, 1918, 340A.

[19] U.S. Pats. 1245981 and 1245982; *J.*, 1918, 340A.

[20] *Analyst*, 1918, **43**, 317; *J.*, 1918, 630A.

[21] *Olien und Vetten*, 1917, **2**, 23, 58, 80; *Z. angew. Chem.*, 1918, *Ref.*, 142; *J.*, 1918, 382A.

The Properties of Pigments and Paints.

M. Luckiesh[22] discusses the value of an analytical method of considering technical problems in colour. The colour value of the illuminant used is the first factor, and it should be considered almost as part of the coloured medium. This point is illustrated by curves showing the spectral reflection factors of ultramarine blue and its spectral luminosity for skylight, sunlight, and the light of a tungsten vacuum lamp. There are three principal methods in use for the analysis of colour. The most analytical is by means of the spectrophotometer, which determines the reflection or transmission factors of the colour for all wave-lengths of the visible spectrum. By combining these factors with the corresponding spectral values of the illuminant and the visibilities of radiation the spectral luminosity curve is obtained. The monochromatic colorimeter expresses the value of a colour in terms of its dominant line, its percentage of saturation (= unity minus percentage white), and a transmission of reflection factor. The trichromatic colorimeter is based on the Young-Helmholtz theory. In considering pigments the reflection factor curves are given for a number of dry powders. Further sections deal with dyes and coloured glasses, and with the laws of combination and of variation of colour with thickness for both of these substances.

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[22] *Met. and Chem. Eng.*, 1917, **17**, 631; *J.*, **1918**, 64A.

The discoloration of white paint and enamel has doubtless exercised the minds at some time or another of most of those concerned in their manufacture. With some enamels, at any rate, this discoloration has, in the writer's experience, been most marked on that part of the surface which is protected from the light—such as behind picture-frames, &c. A paper dealing with this subject is contributed by D. F. Twiss,[23] in which it is stated that this tendency was especially noticed when the painted articles were stored in a fairly warm situation, the result being much the same whether the painted surface was exposed to the light of an ordinary room or kept in the dark. The experiments were made with enamel or paint made from an oil varnish and zinc oxide. It was shown that the discoloration was not due to the presence of lithopone as an adulterant, neither did exposure of dried films to hydrogen sulphide induce any greatly accelerated colour change. The discoloration was mainly confined to the outer surface of the films, while the under-side against the painted article was only slightly affected. After it had been shown that the trouble did not lie with the pigment, attention was turned to the medium, where the seat of the trouble was located, and experiments to substantiate this point are described. Tests were carried out as to conditions under which the discoloration could be removed. It was found that the presence of air as well as light (for convenience a mercury vapour lamp was used) was essential, as discoloured films sealed in a glass tube in an atmosphere of carbon dioxide and exposed to the rays did not lose their discoloration. When exposed to the air, however, they were bleached by the rays. These bleached films could again be discoloured by keeping in a warm place, and these processes could be repeated many times in succession. Poppy-seed oil has less tendency to cause discoloration than linseed oil. No explanation is offered as to the cause of the discoloration other than that it is apparently independent of oxidation and polymerisation of the oil, and is probably due to some minor ingredient of the oil. In connection with this matter the writer of this report found in 1913 that the linseed oil being imported from a certain country stained zinc oxide so yellow that it was impossible to use it for white paints. It was discovered, however, that the staining property of the oil could be destroyed by heating to 200° C.

R. E. Kreher[24] patents a method for making a white-lead pigment by heating in a blast-furnace a mixture of lead-bearing materials, metallic lead in the form of flakes, a flux, and fuel. The vapour produced is condensed and the pig-lead tapped off and poured into a stream of water to flake it for subsequent use. J. A. Singmaster and F. G. Breyer[25] patent the preparation of a zinc-lead pigment containing 65–97% of zinc oxide, and stated to possess a covering power, opacity, flow, and whiteness equal to that of "XX brand of American process zinc oxide." It is obtained by volatilising at a high temperature the zinc and lead from an oxidised ore and subjecting the product to a regulated sulphating and oxidising atmosphere, so that all the lead is converted into sulphate to the required degree without materially sulphating the zinc or unduly maintaining the fume at an elevated temperature. P. Comment[26] patents a method for the preparation of anhydrous zinc sulphide, in which zinc persulphide is employed. Dehydrated and finely powdered zinc sulphate is intimately mixed with sodium or potassium sulphate, or a mixture of the two, and zinc persulphide in the proportions given by the equation :

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[23] *J.*, 1918, 179T.

[24] U.S. Pat. 1248501; *J.*, 1918, 65A.

$$2ZnSO_4 + ZnS_5 + 2Na_2SO_4 = 3ZnS + 2Na_2SO_4 + 4SO_2 .$$

The mixture is calcined at about 800° C., protected from the air, until decomposition of the zinc persulphide is complete, the zinc sulphide washed free of alkali sulphate and dried at 100°–120° C. The method for the preparation of the zinc persulphide is described. In order to obtain lithopones, barium sulphate may be added in any desired proportions.

As is well known to colour-makers, one of the principal disadvantages possessed by lithopone is the change of colour owing to the action of sunlight. The intensity of the change (from light slate grey to black) varies with different brands, and the nature of the vehicle employed in the paint appears to affect the degree of colour produced. To produce a lithopone unaffected by light, G. Rigg[27] decomposes the zinc sulphate therein, *e.g.*, by grinding the lithopone with barium nitrate so as to convert the zinc sulphate into zinc nitrate and barium sulphate. The second method is to treat the calcined lithopone—after removal of soluble constituents—with barium sulphide to convert the remaining zinc sulphate into sulphide.

Further patents have been granted for titanic oxide pigments,[28] various methods being described for the treatment of titanium oxide or hydroxide to render it suitable for use as a pigment.

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[25] U.S. Pat. 1257136 ; *J.*, 1918, 251A.

[26] Eng. Pats. 106489 and 114407 ; *J.*, 1918, 273A, 313A.

[27] U.S. Pats. 1260811 and 1260812 ; *J.*, 1918, 340A.

[28] Eng. Pat. 104885; *J.*, 1918, 250A. Ger. Pat. 303458 ; *J.*, 1918, 383A Eng. Pat. 110535 ; *J.*, 1918, 520A.

In Volume II. of these Reports (p. 330) a litharge-glycerol cement was described. Th. Goldschmidt[29] claims an improvement by using glycol in place of glycerol. A mixture of 75% of litharge and 25% of glycol is stated to yield a product which hardens in one or two hours, whilst a mixture of 90% litharge and 10% glycol sets still more quickly.

The preparation of a rust-proofing composition is the subject of a patent by W. R. Emig.[30] Burgundy pitch is melted, boiled Chinese wood oil added, and the mixture heated to boiling-point. Finely divided iron and phosphoric acid are then added and the mixture stirred till effervescence ceases.

S. Tamari[31] patents a method for preparing an acid-proof composition by adding gradually, with thorough stirring, about three parts of graphite to one part of melted sulphur, raising the temperature of the mixture to about 170° C. and cooling. The composition is applied hot.

A submarine paint is patented by L. S. Tarrant[32] composed of defibrinated animal blood, linseed oil, resin, and pigment.

A paint described by R. Illemann and J. A. Montgomerie,[33] which is miscible with water and yields a waterproof coating, is obtained by adding to a mixture of one part of pitch (or bitumen) and one part of hot tar, a liquid suspension of one part of clay and one part of water. The mixture is heated with agitation to ensure incorporation, but without draining off the water. Agitation is continued until cold. Colouring matters are added as desired.

There are two principal varieties of paint "removers," each having disadvantages. One is based on caustic soda, and the other contains inflammable spirits. It is quite possible to produce a satisfactory article free from the defects possessed by either of the above varieties. No patents or literature on these lines have been noted, but C. McAdam[34] describes one of the second variety based on cresol emulsified with alcohol, acetone, celluloid, gum camphor, and spermaceti.

Natural Resins, Colophony, Ester Gums, and Turpentine.

The resin in pine-wood is rendered insoluble to a great extent by seasoning, according to C. G. Schwalbe and W. Schultz.[35] The longer a wood is kept—particularly in the form of sawdust—the smaller is the quantity of resin that can be extracted, even by a series of different solvents used successively. This fact explains the varying quantities of fat recorded as being present in the resin. The same authors state [36] that pine-wood yields about 11·4% of resin containing 2·7% of fatty acids as determined by the Twitchell method; the heart-wood gives 16% of crude resin containing 3·5% of fatty acids, and the sap-wood 2·4% of resin containing 1·2% of fatty acids.

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[29] Ger. Pat. 302852; *J.*, 1918, 341A.
[30] U.S. Pat. 1263395; *J.*, 1918, 383A.
[31] Eng. Pat. 107370; *J.*, 1918, 188A
[32] U.S. Pat. 1247901; *J.*, 1918, 65A.
[33] Eng. Pat. 117785; *J.*, 1918, 554A.
[34] U.S. Pat. 1274430; *J.*, 1918, 663A.
[35] *Z. angew. Chem.*, 1918, 31, 125; *J.*, 1918, 432A.

D. J. Ogilvy [37] patents a process for extracting resins, &c., from resinous woods by boiling the finely divided wood with a mixture of water and volatile solvent for resins and oils. The mass of resinous and oily constituents which separates is distilled to remove the lighter turpentines and oils. The amount of volatile solvent used should be greater than the proportion of natural solvent in the wood. J. S. Maclaurin's process [38] for separating resins from impurities consists in agitating the resin with an aqueous solution of salt, the sp. gr. of which is greater than that of the resin but less than that of the impurities. Air is then admitted and the agitation continued for two or three minutes, after which a vacuum is created and the agitation renewed. After setting, the resin is withdrawn from the upper part of the mass and washed free from salt.

Siamese gum benzoin has been examined by A. Zincke and H. Lieb,[39] who state that treatment with sodium hydroxide solution yields the sodium derivative of siaresinol, $C_{30}H_{47}O_4Na, 8H_2O$, $[\alpha]_{21}^{D} = + 34{\cdot}97°$, from which siaresinol $C_{30}H_{48}O_4$, $[\alpha]_{22}^{D} = + 27{\cdot}31$ (in methyl alcohol), is liberated by hydrochloric acid, this substance being probably identical with the benzoresinol of Lüdy. With acetic acid siaresinol yields an additive compound, $C_{30}H_{48}O_4, C_2H_4O_2$, crystallising in prisms, m.pt. 280°–281·5° C., whilst the sodium derivative reacts with benzoyl chloride giving a benzoyl derivative, $C_{37}H_{52}O_5$, crystallising in needles, m.pt. 182°–183° C., $[\alpha]_{20}^{D} + 30{\cdot}0$ in ethyl alcohol.

In a further paper [40] the same authors state that, contrary to the opinion of Lüdy, the resinol obtainable from Siamese gum benzoin is not identical with that from the Sumatra variety. Whereas the former resin is incompletely soluble in hot dilute sodium hydroxide solution, the latter is completely soluble, although on boiling the solution for an hour, colourless needles separate of a lævo-rotatory sodium salt of a previously unisolated *l*-benzoresinol, m.pt. 339°–341° C.,

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[36] *Chem.-Zeit.*, 1918, **42**, 229; *J.*, 1918, 382A.

[37] U.S. Pat. 1264551; *J.*, 1918, 433A.

[38] U.S. Pat. 1260984; *J.*, 1918, 340A.

[39] *Monatsh. Chem.*, 1918, **39**, 95; *J.*, 1918, 520A.

[40] *Monatsh. Chem.*, 1918, **39**, 219; *J.*, 1918, 663A.

$[a]_{7}^{D} = -12{\cdot}88°$, *probably of the composition* $C_{29}H_{44}O_4$. On the addition of ether to the mother liquor there is obtained a deposit of the sodium salt of a dextro-rotatory resinol $C_{30}H_{48}O_4, H_2O$, crystallising in needles, m.pt. 298°–299° C., $[a]_{9}^{D} = +51{\cdot}60°$, to which the name *d*-sumaresinol is given and which is isomeric with siaresinol. The benzoresinol of Lüdy from the Sumatra gum was probably merely a mixture of *d*-sumaresinol and *l*-benzoresinol.

Instead of the usual method of reducing the tackiness of resin by fusion with lime, C. Ellis [41] protects a process for treating a solution of the resin in a hydrocarbon inert to hydrogen, with arsenic-free hydrogen at about 10 lb. pressure, in the presence of a nickel catalyst at a temperature above that of the decomposition of nickel acetate.

J. Tausz [42] communicates a paper on the determination of turpentine and the detection of adulterants. The determination is based on the oxidation or combination of turpentine with mercuric acetate, one molecule of acetic acid being set free for each molecule of terpene or other unsaturated hydrocarbon present. Ten c.c. of pure turpentine and 10 c.c. of the sample under examination are each diluted with methyl alcohol to 100 c.c. in order to speed up the reaction. Ten c.c. of each of these solutions is mixed with 50 c.c. of saturated mercuric chloride (? acetate) solution (in methyl alcohol) and 50 c.c. of $\frac{N}{10}$ potassium hydroxide solution (in methyl alcohol). The mixtures are diluted with 100 c.c. of water, shaken, kept in the dark for 1 hour, phenolphthalein added, and sodium chloride solution run in until a red coloration develops; the mixtures are then titrated with $\frac{N}{10}$ sulphuric acid. A control test without turpentine is made at the same time. Usually turpentine substitutes do not react with mercuric acetate; rosin spirit yields a small quantity of free acetic acid, and if this adulterant is present, turpentine containing approximately the same quantity as the sample should be used for the comparison titration. When pure turpentine is heated under a reflux condenser for 3 hours with mercuric acetate solution and methyl alcohol and then distilled with steam, no trace of oil is found in the distillate. Hydrocarbons, however, such as mesitylene, cumene, cymene, petroleum spirit, &c., pass almost quantitatively into the distillate and their quantity may be measured.

The method may be used quantitatively by acting on a methyl alcohol solution of the sample with saturated mercuric acetate solution in a closed flask on a water bath for 4 hours. After cooling, the mercurous acetate formed is collected, washed with alcohol and ether, dried, dissolved in nitric acid (1 : 1), the solution treated with sodium chloride, and the mercurous chloride collected and weighed. A control test is made at the same time, using pure turpentine; the quantity of turpentine in the sample is proportional to the amount of mercurous chloride found.

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[41] U.S. Pat. 1249050; *J.*, 1918, 65A.

[42] *Chem.-Zeit.*, 1918, 42, 349; *J.*, 1918, 554A.

Synthetic Resins.

A further number of patents [43] have been granted for the manufacture of synthetic resins of the phenol-formaldehyde type. These appear to consist of modifications of the original methods, the specific features being as follows: the reaction taking place in the presence of carbon dioxide; the use of hexamethylenetetramine and a current of carbon dioxide; the use of a fusible cyclic hydrocarbon of high boiling-point, soluble in water; the addition prior to the application of heat of a salt of calcium and a phenolic substance which will not react with the other ingredients; the use as condensing agents of neutral salts of aromatic hydroxy-carboxylic acids, such as sodium salicylate; and the use of paraformaldehyde with a tannin condensing agent having no deleterious effect upon the dielectric strength or stability of the resulting product, *e.g.*, catechol-tannin.

In spite of the statements in the last volume of these reports (p. 333) that the cumarone and para-indene resins had been found unsatisfactory, a further series of patents appears during the year. J. P. A. McCoy [44] prepares a chlorine di-substitution product of a resinous coal-tar derivative containing cumarone, indene, para-cumarone, and/or para-indene, by passing gaseous chlorine for about 8 hours through a coal-tar derivative containing at least one of the above-named substances. F. W. Sperr [45] manufactures resins from compounds of this group by subjecting them to heat and a pressure of 50–300 lb. per sq. inch, or by subjecting a solution of such compounds to heat and pressure, then distilling and blowing a gaseous fluid through the heated residue. C. Ellis and N. L. Foster [46] treat liquid aromatic hydrocarbons containing cumarone and indene with a polymerising agent such as sulphuric acid. The unchanged liquid is removed and the soft resinous mass freed from the more volatile constituents by distillation, leaving a hard resin.

S. Langguth [47] prepares a shellac substitute by evaporating the residue of an alcoholic extract of resinous condensation products formed in the manufacture of α- and β-naphthols.

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[43] U.S. Pats. 1253261, 1253262, 1253404, 1259472–3, 1263031. Eng. Pat. 117857. U.S. Pats. 1269627, 1273967; *J.*, 1918, 158A, 158A, 158A, 313A, 383A, 554A, 554A, 663A.

[44] U.S. Pat. 1245363; *J.*, 1918, 14A. [45] U.S. Pat. 1263813; *J.*, 1918, 433A.

[46] Eng. Pat. 117016; *J.*, 1918, 554A. [47] Ger. Pat. 302742; *J.*, 1918, 340A.

INDIARUBBER.

By D. F. Twiss, D.Sc., F.I.C.,
Chief Chemist, Dunlop Rubber Co., Birmingham.

The literature dealing with the chemistry of indiarubber during 1918 has been notably irregular in its distribution over the various sections of the subject. Very few academic investigations have been published, and even the subject of synthetic rubber has received surprisingly little mention, although doubtless this does not justly reflect the extent of the work which has been done, particularly in Germany.

During the year the publication of the translation of the Communications[1] of the Netherlands Government Institute for Advising the Rubber Trade and the Rubber Industry from the Dutch original of 1916 has been completed by the appearance of parts V., VI., and VII. Such collections of original papers in systematic arrangement are greatly to be desired, because of the wider outlook and better-balanced account which they present, and it is to be hoped that not only will further compilations be issued from the same source, but that, where possible, the method may be imitated by other institutions and laboratories engaged in rubber research. A marked feature in the literature of the last few years has been the unusual number of summaries dealing with the chemistry of the rubber industry from various points of view;[2] amongst these summaries may be included the translation of A. Dubosc and A. Luttringer's book on "Rubber, its Production, Chemistry and Synthesis," which reviews the literature up to the year 1914.[3]

Statistics.

At the time of the completion of this report the figures for the year's output of rubber are not complete, but the monthly figures, as far as they are available, indicate that for the major portion of the year the total production is about the same as for the corresponding period in 1917, whilst the output of wild Parà rubber shows a distinct decrease. The estimated output for the whole year is given below, together with the figures for several preceding years;[4] the abrupt termination of the series of large annual increases in the world's production is striking, and the estimated total lies nearer the total for the preceding year than for any other two consecutive years since 1910.

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[1] See "Annual Reports," 1917, 341.

[2] See, for example, *Met. Chem. Eng.*, 1916, 1917, and 1918.

[3] See *J.*, 1918, 350B.

Year.	Plantation.	Brazil.	Rest.	Total.	Percentage increase on preceding year.
1910 . .	8,200	40,800	21,500	70,500	+ 1·2
1911 . .	14,419	37,730	23,000	75,149	+ 6·5
1912 . .	28,518	42,410	28,000	98,928	+ 31·6
1913 . .	47,618	39,370	21,452	108,440	+ 9·6
1914 . .	71,380	37,000	12,000	120,380	+ 11·0
1915 . .	107,867	37,220	13,615	158,702	+ 31·8
1916 . .	152,650	36,500	12,448	201,598	+ 27·0
1917 . .	204,251	39,370	13,258	256,879	+ 27·4
1918 * . .	210,000	38,000	12,000	260,000	+ 1·2

* Estimated.

On account of the present magnitude of the rubber plantation industry the useful disposal of the large crop of rubber seeds has become a matter of considerable economic interest, and a survey of the situation has recently been given by F. G. Spring and F. W. F. Day;[5] the seeds yield a good proportion of oil, which shows considerable promise as a substitute for linseed oil.

Production of Raw Rubber.

Owing to the increased difficulty of transhipment from the plantations and from Brazil it is natural that the attention of various countries should still have been attracted towards the possibility of the home-production of raw rubber. The serious consideration of possible new sources of rubber in Central Europe, to which reference was made in the Annual Reports for 1917 (p. 340), has been extended to the sap obtained from plants of the species *Euphorbia Cyparissias* and *Tithymalus Peplus*;[6] from this, carbon tetrachloride and similar solvents can extract a mixture of rubber and fatty matter, the former being then separable by precipitation with alcohol; by a mathematical calculation it is shown that cultivation of the latter type of plants offers considerable promise as an industry for the production of rubber and "fats." Similarly in America the development of the plantation system in connection with the production of Guayule rubber has been called into further consideration,[7] and the "giant rabbit bush" (*Chrysothamnus*) and "dwarf rabbit bush" (*Ericameria*), containing respectively 6–7% and 10% of resinous rubber, have also been seriously proposed as sources of this important raw material.[8] Under the prevailing circumstances the de-resination of low grade rubbers assumed a renewed attractiveness, and an interesting account of various processes for effecting this operation has been published during the year.[9]

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[4] "The World's Rubber Position," November 1918; W. H. Rickson & Son, London.

[5] *Agric. Bull. F.M.S.*, 1918, **6**, 321; *J.*, 1918, 381A.

[6] *J.*, 1918, 397R.

Of much more serious import than the discovery of new types of rubber-producing plants have been the especially favourable conditions which have obtained in parts of Europe for the encouragement of the production of synthetic rubber on a large scale. It would be difficult to imagine a situation offering greater advantages to a synthetic rubber industry, and the circumstances have called for a close examination as to the stability of the foundations of the plantation rubber industry. In a discussion of the economic botany of rubber production J. B. Farmer[10] has made an interesting comparison of the relative possibilities of the plantation and the chemical factory as sources of this commodity. The main raw materials of the rubber-producing tree, viz., carbon dioxide and water, are abundantly available, and the sunlight which actuates the natural processes of the plant can be utilised freely, whereas for the synthetic production of rubber the raw materials and the processes are relatively expensive. The conclusion is drawn that with careful development of the scientific side of the plantation industry—*e.g.*, the investigation of soil problems, the combating of various fungus diseases, and the careful selection of seed so as to increase the disease-resisting and rubber-bearing qualities—the natural method of producing rubber should be able to maintain its position indefinitely. In support of this argument is quoted the case of the sugar beet, in which by careful work the yield of sugar has been doubled in a period of thirty years. Sanguine comparisons of the prospects of synthetic rubber with the achievement in the commercial synthetic production of indigo are likely to be misleading, because not only did the subsequent application of scientific method give a renewal of vigour to the indigo plantation industry, but also because the chemical synthesis of a crystalline substance such as indigo should be a much simpler matter than that of a colloid of unknown molecular weight, and of which the molecular structure is not finally decided. The limited measure of success attained with synthetic rubber even under the favourable unnatural conditions recently prevailing in Germany was implied in a lecture by C. Duisberg before the German Bunsen Society for Applied Physical Chemistry,[11] in which acknowledgment was made of the difficulty of adapting the product to soft rubber goods, although its application to more rigid articles, such as solid tyres and vulcanites, appears to have been satisfactorily accomplished. That great advances have been made in the large scale manufacture of synthetic rubber is evident from the fact that a single factory has been built at Leverkusen to supply 2000 tons yearly, but there is no question at present of synthetic rubber competing generally with plantation rubber in the open market, and F. Hofmann's demand of a period of thirty-six years [12] for the successful commercial development of the manufacture to a magnitude equal to that of the plantation industry does not appear likely to prove excessive. The fact that during the last year or so the investigations emanating from the plantations and from laboratories associated with them outnumber those dealing with any other section of the chemistry of rubber renders it evident that the rubber growers are not likely to lapse into any passive state towards the competitive rubber synthetists.

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[7] A. H. King, *Chem. Met. Eng.*, 1918, **19**, 23; H. C. Pearson, *Indiarubber World*, 1918, **58**, 579.

[8] *Indiarubber World*, 1918, **58**, 517.

[9] A. H. King, *Chem. Met. Eng.*, 1918, **19**, 141, 203.

[10] *J. Roy. Soc. Arts*, 1918, **66**, 490; see also E. Wheeler, *J.*, 1918, 307T; F. Dannerth, *Indiarubber J.*, 1918, **55**, 134.

Latex and its Coagulation.

The gradual alteration in the characteristics of latex from a freshly tapped tree has been subjected to investigation by O. de Vries,[13] who finds that the rubber content decreases from 44·0% on the first day to a fairly constant proportion of 25–26% after a fortnight, the specific gravity increasing from 0·9689 to 0·9920 for the undiluted latex or from 0·9895 to 0·9950 referred to latex diluted to a 15% rubber content. The rubber prepared by standard methods from the adjusted latex, when vulcanised under the optimum conditions, had an almost constant tensile strength, but the rate of vulcanisation was much slower for the rubber from the first runnings of latex; the rate, however, gradually increased and within a month of tapping became approximately normal; the "slope,"[14] or resistance to stretching at higher loads, showed a simultaneous increase. When the same tree was pollarded at a height of three feet from the ground the rubber content of the latex suddenly dropped to 21% and the specific gravity rose to 0·9960 and 0·9970 for the raw and diluted latex respectively, but a condition of equilibrium was attained in a few days; the alteration in the physical qualities of the rubber was too small to have any technical significance. Heavy tapping also causes a marked decrease in the rubber content of the latex, which may drop even below 17%, the specific gravity rising to 0·9982.[15]

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[11] See *Board of Trade J.*, Sept. 26, 1918; *Indiarubber J.*, 1918; *Chem. Trade J.*, **1918, 162.**

[12] *Z. angew. Chem.*, **1912, 25, 1462**; *J.*, **1912, 693.**

[13] *Comm. Central Rubber Stat., Buitzenzorg, Java*, **1918, 2, 241**; *J.*, **1918, 663A.**

Renewed attention has been given during the year to the effect of the various chemicals used in the preparation of plantation rubber.[16] Crystalline sodium sulphite and sodium hydrogen sulphite, which are used as "anti-oxidants," in the proportion of one gram per litre of "15% latex" cause a slight increase in tensile strength and in the rate of vulcanisation and a slight improvement in the "slope" and viscosity index of the finished rubber, the effect being distinctly more marked for smoked sheet than for pale crêpe; formalin, which is also an "anti-oxidant," on the other hand has an opposite effect, but with 0·5 c.c. per litre of latex the deterioration, although discernible, is within the natural limits of variation for plantation rubber. Crystalline sodium carbonate, applied as an "anti-coagulant," occupies an intermediate position with respect to sodium sulphite and formalin and its influence on the properties of the rubber is exceedingly small. As sodium acetate and sulphurous acid are formed from the sulphite and acetic acid used in the ordinary coagulation process, their effect is also of importance; sodium acetate causes a slight increase in the viscosity and in the rate of vulcanisation, whereas sulphurous acid applied as a coagulant yields a rubber of the same rate of vulcanisation as the acetic acid product but of improved viscosity, tensile strength, and slope; it is indeed likely that the influence observed with sodium sulphite and bisulphite is to be attributed to the joint effect of the sodium acetate and sulphurous acid to which they give rise. It is noteworthy that the antiseptic action of the sodium hydrogen sulphite or sulphurous acid in checking decomposition of the protein matter will tend to prevent any increase in the rate of vulcanisation from this cause, and the improvement observed above must be due to a specific chemical influence in excess of the contrary anti-putrefactive effect. This concurrence of two opposed effects may explain the somewhat different results obtained with sodium hydrogen sulphite by B. J. Eaton.[17] In any case it is of interest to note that a method for the coagulation of latex with sulphurous acid, which may be introduced as sulphur dioxide or as an aqueous solution, has been patented independently.[18]

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[14] P. Schidrowitz, *J.*, 1915, 842; G. S. Whitby, *J.*, 1916, 495.

[15] O. de Vries, *Comm. Centr. Rubber Stat. Buitzenzorg*, 1918, 2, [No. 9], 437.

[16] *Ibid.*, 1918, No. 6, 1, No. 9, 456; also *J.*, 1917, 140.

The threatened shortage of acetic acid for use on the plantations has caused additional attention to be given to the possibilities of natural or spontaneous coagulation. In a review of some of the problems facing the plantation industry H. P. Stevens [19] has weighed the relative merits of the acetic acid and the spontaneous coagulation processes, with the result that the latter method is believed to possess the advantage of yielding a more uniform product. M. Barrowcliff, discussing the preparation of "standard plantation rubber," has examined the reasons for the greater uniformity of Fine Hard Parà rubber relative to the plantation product,[20] and makes a claim that the method introduced by M. D. Maude and W. S. Crosse (the so-called M.C.T. process),[21] employing spontaneous coagulation for the separation of the rubber from latex under the anaërobic conditions produced by the carbon dioxide evolved, yields a rubber which, in its degree of uniformity, is superior to any other form of plantation rubber; in rate of vulcanisation the product of spontaneous coagulation is comparable with smoked sheet, being therefore a little more rapid than pale crêpe or Fine Hard Parà.

The mechanism of spontaneous coagulation, to which reference was made in the Annual Reports for 1916 (p. 199), has been the subject of further discussion. B. J. Eaton adheres to the view that the coagulative agent is lactic acid produced from the natural sugars of the latex by bacterial action,[22] and quotes in support of his theory the investigation of the micro-organisms of latex by Denier and Vernet.[23] The rival theory that spontaneous coagulation is essentially due to an enzyme present in the latex has been strengthened by M. Barrowcliff; [24] the period necessary for spontaneous coagulation is less than would be expected if this were dependent on the bacterial formation of lactic acid, and toluene and thymol, which as antiseptics are fatal to most micro-organisms but do not harmfully affect enzymes, fail to retard the natural coagulation of latex, whereas hydrocyanic acid, which is fatal to almost all enzymes, completely inhibits coagulation. The fact that the calcium salts naturally present in small quantity in latex exert a considerable influence on the coagulation process,[25] which is greatly retarded by their removal, has a noteworthy parallel in the similar effect of small quantities on the activity of enzymes. Sterilised latex does not behave normally with the usual small proportion of acetic acid, but the addition of a little fresh latex causes coagulation to occur in a perfectly normal manner; this behaviour suggests that also in the present processes ordinarily adopted for the coagulation of *Hevea* latex the action is probably enzymic, the small amount of acetic acid, from the smoke in the Brazilian process or introduced as such on the plantations, serving to activate the enzyme already in the latex and not acting *per se*. The comparison between the coagulation of latex and the clotting of milk which is drawn in this paper has been considerably extended by G. S. Whitby,[26] who also lays stress on the difference between the phenomena in the clotting of milk by acids and rennet respectively. Below a certain small concentration, acetic acid and lactic acid actually exert an anti-coagulative effect as compared with untreated milk, this result being attributable to the inhibition of the growth of the lactic acid bacterium and of the consequent development of further acidity; on the other hand, acids at all concentrations accelerate the coagulation of *Hevea* latex, the effect merely being feebler at greater dilution. The clotting of milk by acids is almost instantaneous, whereas that of latex is gradual, requiring from several minutes to several hours, the period being comparable with that required for the "setting" of milk by rennet, whilst, in appearance, the coherent clot formed in the last case more closely resembles the ordinary rubber coagulum than the flocculent precipitate obtained from acidified milk. Although small quantities of hydrochloric or nitric acid cause latex to coagulate, with a larger proportion a neutral point is reached at which no such effect is observed, the acid at this concentration possibly producing a paralysis or destruction of the enzyme; at still higher concentrations these acids again exhibit coagulant properties, due presumably to the well-known effect of acidic substances on negative colloidal suspensions, the phenomenon then probably being identical with that observed by V. Henri in the coagulation of dialysed latex with solutions of acids of semi-normal concentration.[27] The evidence seems so circumstantial as to justify the claim that the initial formation of the coagulum in fresh latex allowed to undergo natural change, is due to enzymic action, and that the same agency activated by acid is responsible for the customary coagulation with acetic acid. A process covering the separation of rubber from latex with the aid of the enzyme "coagulase" has been patented.[28]

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[17] *Agric. Bull. F.M.S.*, 1918, **6**, 315; *J.*, 1918, 630A.

[18] Lintner & Co., Eng. Pat. 108298; *J.*, 1918, 131A.

[19] *J.*, 1918, 237R.

[20] *J.*, 1918, 95T; also B. J. Eaton, *Indiarubber J.*, 1918, **55**, 162; and *J.*, 1916, 715.

[21] G. M. Thomas and M. D. Maude, Eng. Pat. 104323; *J.*, 1917, 465.

Agric. Bull. F.M.S., 1915, **4**, 28; *J.*, 1916, 263; *Agric. Bull. F.M.S.*, 1917 **5**, 48; *J.*, 1918, 99A.

[23] *Comptes rend.*, 1917, **165**, 123; *J.*, 1917, 970.

[24] *J.*, 1918, 48T, 262T.

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[25] L. E. Campbell, *J.*, **1917**, 274.

[26] *Agric. Bull. F.M.S.*, **1918**, **6**, 374; *J.*, **1918**, 708A.

[27] *Comptes rend.*, **1907**, **144**, 431; *J.*, **1907**, 265.

The shortage of acetic acid has also revived the interest in alternative coagulants, and experiments have been made with crude pyroligneous acid and with the acidic liquor obtained by passing smoke from *Hevea* wood through water;[29] using these diluted to the standard degree of acidity, rubber was obtained of fairly normal appearance but inferior to ordinary crêpe rubber in rate of vulcanisation, this difference being ascribed to the effect of the formaldehyde and phenolic substances also present in the coagulant (comp. p. 302); a similar retarding effect is well known to accompany the preservative action of the smoke in the production of Brazilian rubber. Other possible coagulants on which unfavourable comment has fallen recently are hydrofluoric acid, sulphuric acid, sodium hydrogen sulphate, alum, and fermented coconut milk.[30]

Non-Caoutchouc Constituents of Latex.

In a discussion of the variability in the yield of finished rubber from latex of constant rubber content, O. de Vries and H. J. Hellendoorn show that the loss of rubber due to the formation of a milky serum must be relatively slight and that the irregularities observed are mainly caused by differences in the percentage of non-caoutchouc serum substances retained.[31] A modified coagulation process intended to ensure the retention of the whole of the serum substances has been proposed, involving the addition of a small quantity of boric acid or other reagent by which the protein ingredients may be rendered insoluble, before coagulation of the rubber is effected; the resulting coagulum is stated to contain all the nitrogenous matter of the latex uniformly dispersed throughout its mass, and to be free from slime and the tendency to darken or become mouldy, whilst the finished rubber has improved physical characteristics.[32]

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[28] E. M. Slocum, U.S. Pat. 1268639; *J.*, 1918, 631A.

[29] B. J. Eaton and G. S. Whitby, *Agric. Bull. F.M.S.*, 1917, 5, 124; *J.*, 1918, 99A.

[30] B. J. Eaton, *Agric. Bull. F.M.S.*, 1917, 5, 48; 1918, 6, 315; *J.*, 1918, 99A, 630A; also *J.*, 1916, 1165. See also *Ann. Rept.*, 1917, 339.

[31] *Comm. Central Rubber Stat. Buitzenzorg*, 1918, 2, 361; *J.*, 1918, 664A.

[32] E. M. Slocum, U.S. Pats. 1259793, 1259794, and 1270887; *J.*, 1918, 313A, and 631A.

The percentage of moisture retained by air-dried rubber prepared in the usual manner is largely dependent on the amount of the serum substances present ; [31] sheet rubber obtained by rolling coagulum whilst still only a few hours old may retain 2–3% of moisture in the air-dried condition, whereas the same sheets after being soaked in water, or similar sheets prepared from diluted latex, may retain as little as 0·3%. Investigation of the dependence of the moisture content of air-dried rubber on the external atmospheric conditions has been made on the actual plantation in Malay by G. S. Whitby ; [33] the results generally confirm those obtained under European laboratory conditions by K. van der Leur ; [34] "dry" crêpe and sheet rubbers suffer a diurnal variation in moisture content ; this is distinctly higher in early morning than in late afternoon, the variation being parallel with the degree of humidity of the atmosphere ; thus rubber containing less than 1% absorbed moisture from the air between sunset and sunrise. The susceptibility of the rubber to the surrounding atmospheric conditions is roughly proportional to the amount of retained serum solids, which are very hygroscopic. It is mainly for this reason that the moisture content of sheet rubber is generally found to be greater than that of pale crêpe under similar conditions.[35]

Recent opinion has been rather divided as to the advantages of "slab" rubber, prepared by allowing the fresh coagulum to mature for several days whereby the protein matter undergoes partial decomposition. The resulting rubber certainly vulcanises much more rapidly, but the further claim that it is more uniform and gives products of much greater tensile strength than ordinary sheet or crêpe rubber is contested by O. de Vries,[36] who finds only a small increase in tensile strength,[37] whilst the rate of vulcanisation is not uniform, being affected by the natural variation in the composition of the latex from different trees and by the degree of dilution. In a fuller examination of "matured slab" rubber than has been made hitherto, it is shown that the "slope" is invariably better and the viscosity slightly higher than for ordinary sheet and crêpe. During the maturing process a loss in weight of 2–2½% is observed due to decomposition of serum substances, and other disadvantages in the product are the poor colour and the increased difficulty of drying. It is of interest that freshly rolled crêpe rubber on immersion in water for several days exhibits distinctly the usual phenomena of "maturing" as observed in coagulum, whereas fresh coagulum placed under water produces a rubber comparable only with ordinary crêpe in rate of vulcanisation.

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[33] *J.*, 1918, 278T.

[34] *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1916, 2, 41 ; *J.*, 1917, 1104.

[35] See also O. de Vries, *Comm. Central Rubber Stat. Buitzenzorg*, 1918, No. 1, 9.

[36] *Comm. Central Rubber Stat. Buitzenzorg*, 1918, 2, 235 ; *J.*, 1918, 664A.

[37] See also Schidrowitz and Goldsbrough, *Indiarubber J.*, 1917, **54**, 162, 184 *J.*, 1917, 971.

Properties of Raw Rubber

It is generally recognised that during the process of mastication, which forms one of the first stages in the treatment of rubber in the factory, much of the moisture of the rubber is expelled. This knowledge indeed has been applied in a method for the prevention of dust during the introduction of fine powders, such as "gas black," into rubber; the powder is previously moistened with kerosene or with water, the latter at any rate being eliminated almost completely during the subsequent "working" of the mixing.[38] It is opportune therefore that attention has been again directed to the fact that normal mastication does not expel the whole of the natural moisture of plantation rubber, and that 0·2—0·3% may be retained after the mastication process;[39] during subsequent vulcanisation, therefore, unless the surrounding pressure is maintained greater than the vapour pressure of the dissolved water, porosity is likely to occur. Soft and under-vulcanised rubbers will be particularly liable to porosity if the external pressure is reduced before the rubber has cooled down and thereby regained much of its normal strength.

The measurement of the viscosity of solutions of raw rubber in benzene has been suggested as a basis for the control of the mastication of rubber and similar operations during the preliminary stages of rubber manufacture.[40] A belief that the "depolymerisation" caused by mastication is attended by a reduction in the proportion of the resinous constituents soluble in acetone appears to be unjustified.[41] Unfortunately the meaning of "depolymerisation" is very indefinite in the present usage of the word by rubber chemists; not only is very little indeed known of the nature of the change above described by this term, but the word is applied to apparently quite distinct phenomena. The development of "tackiness" in rubber is frequently described as depolymerisation, but this change is quite distinct from that produced by mastication. A. van Rossem has demonstrated that, in the sense of the development of tackiness, depolymerisation in raw rubber, whether dissolved or otherwise, is greatly aided by rise of temperature and by the presence of oxygen, and has adduced strong evidence that the effect of the latter is primarily catalytic, oxidation being unessential to depolymerisation and indeed succeeding this change.[42] Copper and its compounds are capable of accelerating in a marked manner the development of tackiness, and their activity has been the subject of numerous investigations.[43]

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[38] W. C. Geer, U.S. Pat. 1245700, 1917; *J.*, 1918, 14A.

[39] G. van Iterson, *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1918, 7, 229; *J.*, 1918, 595A: see also J. G. Fol, *ibid.*, 1917, 4, 113; *J.*, 1917, 1242.

[40] S. Takeuchi, *J. Chem. Ind. Tokyo*, 1917, 20, 1297; *J.*, 1918, 313A.

[41] J. G. Fol, *Gummi Zeit.*, 1917, 31, 761; *J.*, 1918, 341A; K. Kawakami, *J. Chem. Ind. Tokyo*, 1918, 21, 226; *J.*, 1918, 476A.

It is a striking fact that with the exception of the classical work of C. Harries on the behaviour of caoutchouc towards ozone,[44] which demonstrated that the molecule is composed of nuclei of the structure $—CH_2 . C(CH_3) : CH . CH_2-$ linked together into a ring of uncertain dimensions, oxidation processes, on account of the physical nature and chemical complexity of the products, have thrown very little light on the molecular structure of the rubber hydrocarbon, although the results have frequently been of technical importance in connection with the spontaneous oxidation of rubber. S. J. Peachey[45] in 1912 described a convenient arrangement of apparatus for observing the rate of oxidation of a rubber film on the internal surface of a flask, and in experiments at 85° C. was able to show that the presence of the normal resin content exerts a distinct retarding influence, and that absorption of oxygen ceases when the proportion which has gone into combination corresponds with the ratio $C_{10}H_{16} : 4O$. In an extension of this research it is shown[46] that the presence of moisture is not essential to the oxidation process, and that in addition to the solid oxidation product, carbon dioxide is formed in considerable amount approximating to one mol. to $4C_{10}H_{16}$. By exposing a larger quantity of plantation rubber from which the natural resins had been extracted, to air at 85° C. for six months, and extracting the mass daily with alcohol, a solution was finally obtained which on fractional precipitation yielded a brownish yellow neutral viscid resin of the composition $C_{16}H_{26}O_3$, a feebly acidic fawn-coloured powder $C_6H_9O_2$, and a feebly acidic substance $C_{11}H_{16}O_4$, whilst the residual insoluble reddish brown gritty powder had the composition $C_9H_6O_2$. On account of the difficulty of purifying amorphous colloidal substances it is likely that the above formulæ represent the approximate composition rather than the molecular magnitude; this doubt receives some support from the fact that the last-named product on oxidation yields oxalic acid and a yellow powder for which analysis suggests the formula $C_{11}H_{13}NO_6$. The results certainly demonstrate that the natural oxidation of raw rubber is a more complex chemical change than might be expected from the composition of the oxidation products described earlier by J. Spiller[47] ($C_{30}H_{43}O_{10}$) and E. Herbst ($(C_{10}H_{16}O$ and $C_{10}H_{16}O_3)$.[48] Under similar conditions vulcanised rubber undergoes oxidation much less rapidly than unvulcanised, the rate again being increased by the removal of the natural resins; no sulphur dioxide is formed, but carbon dioxide is again produced and, probably because of the relatively small proportion of combined sulphur necessary for vulcanisation, the reacting proportions of rubber and oxygen are approximately the same as for raw rubber, *viz.* $C_{10}H_{16}$: 1O. With purified balata the rate of oxidation is not radically different from that of rubber, although it follows a slightly different curve; the final state, however, indicates that the balata hydrocarbon is of quite distinct constitution and that the mechanism of the oxidation is of another type, the proportion of hydrocarbon to oxygen consumed being $C_{10}H_{16}$: 5O and that of hydrocarbon to carbon dioxide produced being $3C_{10}H_{16}$: CO_2.

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[42] *Rubber Industry*, 1914, 151; *J.*, 1915, 671; *Gummi Zeit.*, 1917, **31**, 851; *J.*, 1917, 1242; 1918, 341A: see also K. Gorter, *Ann. Rept.*, 1916, 206.

[43] *E.g.* Thompson and Lewis, *J.*, 1891, 717; B. J. Eaton, *J.*, 1913, 666; A. van Rossem, *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1917, **4**, 121; *J.*, 1917, 1242; C. P. Fox, *J. Ind. Eng. Chem.*, 1917, **19**, 1092; *J.*, 1918, 99A.

[44] *Ber.*, 1904, **37**, 842; 1905, **38**, 1195, 3985; *Z. angew. Chem.*, 1912, **25**, 1457 *J.*, 1904, 830; 1905, 448; 1906, 33; 1912, 733.

[45] *J.*, 1912, 1103.

S. J. Peachey and M. Leon, *J.*, 1918, 55T.

Vulcanisation.

Several investigations of much interest have been published during the year, dealing with the chemistry of vulcanisation. The sections of the translation of the Communications of the Netherland Government Institute for advising the Rubber Trade and the Rubber Industry, which were outstanding from 1917, have now appeared and are chiefly concerned with this matter. Details are given of the method of testing[49] adopted by the Institute. The standard mixing contains rubber 92½%, sulphur 7½%, and is vulcanised for 1½ hours in steam at 52 lb. or at 148·25° C. It has been found convenient, however, to replace the usual method of heating with steam by the use of an oil bath,[50] in which small moulds of special construction containing the mixing are immersed; on account of the rapid transference of heat, the temperature required to produce the same vulcanising effect in the standard period has to be reduced to 147° C. In order to prevent the development of porosity in the resulting discs of rubber, a small quantity of water is enclosed with the rubber mixing inside the mould. A marked advantage of this method of vulcanisation is that moulds can be removed from the bath or further moulds introduced as desired, without interfering with the progress of the vulcanisation of the samples already immersed. From the result of numerous experiments it is shown that stress-strain curves for different rubbers vulcanised in the standard manner very rarely intersect, and although the final points of curves for different rings of the same mixing may vary, the curves themselves are usually coincident, the position of the actual breaking point being to some extent fortuitous. It is therefore preferable to record the load required to produce a definite elongation rather than the breaking load, and an extension of 850% is arbitrarily selected as standard. The magnitude of the load necessary to produce this elongation is so much more constant than the ultimate tensile strength for rings cut from the same vulcanised slab, that by testing merely one ring it is possible to fix the position and therefore the course of the stress-strain curve. This method of procedure for testing offers considerable advantages in the economy of time and labour apart from material and has received favourable comment from H. P. Stevens, who, however, used a standard mixing containing 10% of sulphur and measured the load at 900% and 1000% elongation.[51] General standardisation of the methods and conditions of testing is urgently needed, and H. P. Stevens recommends that in order to avoid variation arising from irregularity in the physical properties due to the unequal effect of ageing [52] for different periods and different temperatures, specimens should be tested one day after vulcanisation, and that the temperature of storage and also, if possible, of testing should be 30° C.; this would render close comparison possible between results obtained with a similar mixing in North Europe and in the tropics, but it is also highly desirable that the standard mixing should be the same for all rubber-testing laboratories, and unfortunately this is not the case at present.

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[47] *J. Chem. Soc.*, 1865, **18**, 44.

[48] *Ber.*, 1906, **39**, 523; *J.*, 1906, 224.

[49] 1918, **5**, 125; *J.*, 1918, 215A.

[50] A somewhat similar method using a glycerin bath was described by D. Spence and J. Young, *Chem.-Zeit.*, 1912, **36**, 1162; *J.*, 1912, 1043.

As was indicated in Part I. of the Communications of the Netherlands Institute, different rubbers with the standard proportion of sulphur, when vulcanised by the described method to the same degree of vulcanisation generally give approximately coincident stress-strain curves. It is important, however, that information should be available as to the extent to which variation in the conditions of experiment may interfere with this connection between the mechanical properties and the vulcanisation coefficient.[53] Experiments by B. J. Eaton and J. Grantham[54] on the "optimum cure" at different temperatures suggest that the disturbing effect due to variation of temperature may not be very great, but a paper by G. D. Kratz and A. H. Flower, read recently before the Rubber Section of the American Chemical Society and describing an investigation directed to observe the effect of the temperature of vulcanisation on the relation between the mechanical properties of the product and its proportion of combined sulphur, should be of particular interest.[55] The relative simplicity of the relationship between the percentage of combined sulphur and the mechanical properties of standard mixings vulcanised under the same conditions is adversely affected by the presence of artificial organic catalysts, such mixings showing a reduced extensibility, *i.e.*, a "stiffer" character than the corresponding simple rubber-sulphur mixing of the same vulcanisation coefficient, although the limit of elongation is not reduced; even the natural accelerators developed in "matured slab" rubber produce this effect. Nevertheless in view of the great alteration which can be produced in the mechanical properties of a newly vulcanised rubber sample by ageing, the proportion of sulphur combined with the rubber is probably much more trustworthy and of more significance as an index of the actual state of vulcanisation.[56]

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[51] *J.*, 1918, 208T.

[52] O. de Vries, *Indiarubber J.*, 1917, **53**, 101; *J.*, 1917, 296; *Ann. Repts.*, 1917, 347 also this vol., p. 311.

The alteration in the mechanical properties, or the ageing, of newly vulcanised rubber on storage for a few weeks is not accompanied by any change in the proportion of combined sulphur. If, however, storage is prolonged, an apparent alteration may be observed in the vulcanisation coefficient as determined in the usual manner by extraction of the soluble uncombined sulphur. The alteration is variable in extent, and as also it is not always an increase, although frequently so, doubt must arise as to whether it represents a genuine change in the amount of sulphur combined with the rubber. A conversion of part of the uncombined sulphur into an insoluble form, *e.g.*, by oxidation to sulphuric acid, which is known to be produced during long storage and to be tenaciously retained by rubber, or by transformation into the insoluble modification of sulphur, which is known to be facilitated by contact with acids, would be capable of producing the observed result. The serious alteration in the mechanical properties on storage had been clearly illustrated recently by H. P. Stevens,[57] who by means of a prolonged series of tests shows that the breaking strain and corresponding elongation of rubbers, whether ordinary sheet or "matured slab," with a vulcanisation coefficient exceeding 3, steadily decrease although frequently first attaining a slight transient maximum at the expiry of the first week or so. With higher coefficients the decrease in strength and elongation becomes much more marked, and the results clearly demonstrate the misleading nature of the term "optimum cure" as commonly applied to the temperature and period of vulcanisation which, with a mixing containing 7–10% of sulphur, yield a product of immediate maximum strength.

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[53] H. E. Potts, "Chemistry of the Rubber Industry," p. 100.

[54] *J.*, 1915, 989.

[55] Details not available at the time of writing.

[56] See H. P. Stevens, *J.*, 1918, 156T, 280T; D. F. Cranor, *Indiarubber World*, 1918, 59, 24; *Ann. Repts.*, 1917, 347.

In the experiments recorded, a mixing with a coefficient of vulcanisation 3·1, possessing an initial tensile strength of approximately 2000 and corresponding elongation of 1050, after 120 weeks gave the fairly satisfactory figures 1300 and 925 respectively for the strength and elongation, whereas in a mixing vulcanised to a coefficient of 4·4, the tensile strength and elongation fell from values 2200 and 970 respectively to 100 and 420 respectively. With such striking alterations it is desirable to dissect the various possible influences, *e.g.*, of light, atmospheric oxygen, and temperature. The storage in the experiments quoted was in almost complete darkness, and experiments by O. de Vries [52] have demonstrated the important influence of variation in the temperature in artificially accelerating ageing, but further information as to the extent of the effect of each factor on rubber stored for long periods would be of great value in connection with the "keeping qualities" of manufactured rubber articles under varying conditions. It is important also to bear in mind that the above investigation on deterioration was made with a mixing containing only rubber and sulphur, and that with technical mixings the phenomena may be modified and generally will be less marked.

Although the earlier results of S. Axelrod [58] were suggestive of the contrary, it is now realised that rubber may be subjected to considerably different degrees of mastication without its rate of vulcanisation being affected; [49, 54, 59] the reduction observed in the breaking load and elongation is due merely to a recession of the end point of the stress-strain curve, the actual course of which is unaltered. Heating for several hours in an atmosphere of carbon dioxide, which has already been shown to increase the percentage of the insoluble constituent of raw rubber,[60] also effects a slight increase in the rate of vulcanisation.

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[57] *J.*, 1918, 305T; also 1916, 872.

[58] *Gummi Zeit.*, 1909, **24**, 352; *J.*, 1910, 34.

[59] D. Spence and C. A. Ward, *J.*, 1913, 97.

[60] See *Ann. Repts.*, 1917, 343.

Various results of interest with respect to the chemical kinetics of vulcanisation have been reported.[61] In view of the very different behaviour encountered in simple chemical reactions, it is at first surprising to find that with rubber-sulphur mixings containing 2–10% of the latter, not only is the percentage of sulphur entering into combination in a constant period of vulcanisation proportional to the amount of sulphur originally present, but for varying periods with any one mixing it is approximately proportional to the time; the curve representing the amount of chemical change against the time therefore is roughly rectilinear until almost the whole of the free sulphur has disappeared.[62] With mixings containing more than 10% of free sulphur, which appears to approximate to the limiting degree of solubility of sulphur in rubber [63] at ordinary vulcanisation temperatures, the amount of sulphur entering into combination is no longer proportional to the sulphur content or to the time, and the change-time curve is no longer rectilinear but with increasing amounts of sulphur gradually assumes a pronounced Series 73 form. From these characteristics it is probable that the phenomenon of autocatalysis plays a considerable part in vulcanisation, the autocatalytic effect, which will increase as vulcanisation proceeds, tending to neutralise the retarding effect caused by the gradual disappearance of free sulphur, and actually compensating approximately for this in mixings containing less than 10% of free sulphur. This explanation receives confirmation from the behaviour of mixings with less than 10% of sulphur but containing an additional organic accelerator, either introduced as such or formed, as in "slab" rubber,[64] during the maturing of the coagulum; in such mixings the rate of reaction shows a distinct and steady decrease as vulcanisation proceeds, probably because the chemical side of the vulcanisation process is accentuated by the catalyst and is therefore no longer fully compensated by the autocatalytic effect. Attention was drawn by W. Ostwald [65] in 1913 to the fact that the rate of combination of rubber with oxygen as determined by S. J. Peachey (see p. 308) gives distinct evidence of the occurrence of autoxidation, so that in this respect at least the mechanism of the oxidation process is comparable with that of vulcanisation.

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[61] A. van Rossem, *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1918, **6**, 179: G. van Iterson, *ibid.*, 1918, **7**, 223; *J.*, 1918, 476A, 595A.

[62] D. Spence and J. Young, *J.*, 1911, 817; 1912, 81, 785.

[63] H. Skellon, "Rubber Industry," 1914, 172; *J.*, 1915, 671; *Ann. Repts.*, 1916, 217.

[64] H. P. Stevens, *J.*, 1918, 280T.

[65] *J.*, 1913, 179.

As might be expected, inert fillers, such as flint or pumice, since they do not in reality alter the concentration of the reacting substances, do not affect the rate of vulcanisation although they cause a reduction in the tensile strength and elongation of the product. Soft fillers, such as paraffin wax, have an unfavourable influence on the mechanical properties. Basic substances, as had already been shown, generally accelerate vulcanisation, whereas acidic substances have a retarding influence.

Useful general reviews of the nature of the vulcanisation process have been published in 1918 by A. H. King[66] and G. van Iterson.[67] The latter accepts the fact that during vulcanisation the sulphur becomes definitely "bound" by the rubber, but considers that the evidence as to a limiting combination of 32% corresponding with a compound $C_{10}H_{16}S_2$[68] is not final; it must be remembered, however, that much of the work in this direction has been done with crude natural rubber, which can hardly be expected to give the simple stoichiometrical relation. Attention is also drawn to the remarkable parallel between the relative influence of basic and acidic substances on the equilibrium between the various allotropes of sulphur and on the rate of vulcanisation of rubber. Experiments with plastic sulphur and precipitated colloidal sulphur gave no indication of marked difference in vulcanising power as compared with ordinary sulphur, but it is suggested that this does not disprove the possibility that basic substances act as accelerators by virtue of their influence on the sulphur equilibrium because the above allotropic modifications may have been converted into the common rhombic form during the mechanical working involved in mixing. This explanation, however, is unlikely because, as D. F. Twiss has shown, a rubber-sulphur mixing made with insoluble sulphur[69] retains its sulphur in the insoluble condition and also has a characteristic opaque appearance and pale cream colour.

An examination of the products obtained in the destructive distillation of vulcanised rubber below 240° C. by A. Dubosc[70] possesses interest in that no organic sulphur compounds were detected amongst the volatile products, which included hydrogen sulphide, acetylene, acetic acid, benzene, toluene, xylenes, ethylbenzene, and dipentene.

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[66] *Met. Chem. Eng.*, 1918, **18**, 243; see also W. A. Gibbons, *Indiarubber J.*, 1917, **53**, 573.

[67] *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1918, **7**, 239; *J.*, 1918, 595A.

[68] *E.g.*, see D. Spence and J. Young, *Kolloid Zeits.*, 1913, **13**, 265; *J.*, 1913, 1120.

[69] *J.*, 1917, 789.

[70] *Caoutchouc et Gutta Percha*, 1918, 9617; *J.*, 1918, 709A.

This might be considered favourable to the view that during vulcanisation the fixation of the sulphur is a purely physical process, but as the vulcanised material consisted of the beading of motor covers, which is likely to contain other organic matter than rubber in addition to a high percentage of mineral substances, and as also the last layer of fabric was not removed, very different results might have been obtained with a vulcanised material containing rubber and sulphur only. The same author has also described a method [71] for the treatment of vulcanised rubber with hydrogen chloride; the resulting mixture contains hydrochlorides derived respectively from "polyprene sulphide," from rubber which has become "stabilised" by absorption of sulphur, and from metastable rubber which represents unaltered raw rubber; the last hydrochloride can be dissolved out with chloroform and its proportion is claimed to be a valuable indication of the quality of a "reclaim" or of the suitability of a rubber for "reclaiming." The idea is suggestive but needs fuller investigation.

Accelerators.

Vulcanisation catalysts, which were first introduced in order to render experimental synthetic rubber susceptible to the ordinary vulcanisation process, have now secured a recognised position in the trade lists of chemicals for the general rubber industry; the number of articles quoted for the purpose is apt to be misleading, because in some cases the same chemical substance appears several times under different trade names in the same list. In America, where the use of accelerators appears to be customary, it has been found advisable to appoint a Committee to report on their possible poisonous nature, and the finding [72] is that of the more common accelerators, aniline, hexamethylenetetramine, *p*-phenylenediamine, *p*-nitrosodimethylaniline, and thiocarbanilide, *p*-phenylenediamine is the most and thiocarbanilide probably the least harmful; [73] suggestions are also made as to methods for the protection of the workers.

A comparison of the effect of various inorganic and organic accelerators has been made by H. P. Stevens,[74] the examples selected being litharge, magnesium oxide, *p*-nitrosodimethylaniline, and one described, rather indefinitely, as a "basic amino-derivative." With a mixing containing 10% of sulphur and with a period of vulcanisation of one hour at 138° C., it is found that magnesium oxide, if present, in a proportion not exceeding 0·6–0·7%, is much more powerful than any of the others at the same concentration; litharge is the most feeble. It is, however, important to note that with a gradually increasing concentration the additional activity of the magnesium oxide rapidly decreases; with the organic accelerators the effect is more closely proportional to the concentration, whereas in the case of litharge, increase in the percentage causes a more than proportional rise in the accelerating effect. As the proportion of magnesia or litharge used in practice is commonly greater than that employed in these experiments, further tests with higher percentages of accelerator would be of interest.

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[71] *Caoutchouc et Gutta Percha,* 1918, 9646. C. D. Harries, *J.*, 1916, 747.

[72] *Indiarubber World,* 1918, **59,** 82.

[73] For a fuller list of accelerators see A. H. King, *Met. Chem. Eng.*, 1916, **15,** 231 1918, **18,** 243.

[74] *J.*, 1918, 156T; see also A. van Rossem, *Comm. Netherland Govt. Inst. for advising Rubber Trade,* 1918, **6,** 202; *J.*, 1918, 476A.

In furtherance of his claim for priority in the application of various organic compounds as accelerators, D. Spence has published details[75] of a paper which he had drafted already in 1911. Having recognised that the superiority of certain raw rubbers in rate of vulcanisation is due to the presence of nitrogenous "impurities" which act essentially as catalysts, he had successfully replaced these by organic substances, such as quinine, aniline, *p*-phenetidine, piperidine, thiocarbanilide, alkyl derivatives of lead and of mercury, and oleates of sodium and lead. The assertion is made, without substantiation, that "in America the knowledge of accelerators is so advanced that they are chosen to improve the physical qualities in addition to hastening the rate of vulcanisation; they toughen the rubber and render it immune to deterioration."

It is regrettable that the published investigations as to accelerators leave much to be desired. Many points need elucidation, and as our knowledge of the mode of action of accelerators is so largely empirical it would be advisable at first to test each example separately and more exhaustively than hitherto. Very little definite information is available as to the influence of accelerators on the ageing of vulcanised rubber and still less as to the possible influence of the proportion of free sulphur on the activity of the accelerator. The recently elaborated view of A. Dubosc[76] that only "colloidal" sulphur is capable of vulcanising rubber and that accelerators such as litharge and magnesia increase the rate of vulcanisation by oxidising sulphur to sulphur dioxide, which then reacts with hydrogen sulphide resulting from the interaction of sulphur and the natural resinous and protein matter of the rubber, with formation of the active colloidal sulphur, unfortunately does not accord with the facts.[77] With an elucidation of the mechanism of the action of the catalyst there will arise the possibility of an intelligent selection of an accelerator specifically suited to produce the desired chemical and physical results in the considered mixing.

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[75] *Indiarubber World,* 1918, **57,** 281; see also *Ann. Repts.,* 1917, 351 and *Kolloid Zeit.,* 1912, **11,** 275; *J.,* 1913, 97; 1917, 118.

[76] *Caoutchouc et Gutta Percha,* 1917, **14,** 9109; *J.,* 1917, 296.

Regeneration of Vulcanised Rubber.

The various processes applied to the regeneration or reclaiming of vulcanised rubber do not aim so much at the devulcanisation of the material as at the regeneration of the physical properties to a condition approximating to that of the mixing previous to vulcanisation,[78] Not only have few really serious claims been made as to the removal of the combined sulphur from the rubber, but in some cases it is doubtful whether some of the free sulphur is not actually driven into combination with the rubber during the so-called devulcanisation process. Recently there has been a tendency towards open acknowledgment that the essential effect during "reclaiming" is a thermal one and to simplify matters by dispensing with unnecessary chemical operations. A process recently published from a German source involves merely the heat treatment of the waste vulcanised rubber in an inert atmosphere or in a vacuum, the danger of serious oxidation when the hot rubber is subsequently removed from the hot chamber being avoided by rapid cooling.[79] An apparatus designed for a similar purpose has been patented independently.[80]

What might at first appear to be a highly novel method of reclaiming may actually be merely a modification of the simple thermal treatment. Ordinary waste vulcanised rubber is heated with tellurium or tellurium compounds at temperatures up to 250° C.[81] The chemical relationship of tellurium with sulphur and selenium, which are capable of vulcanising rubber, gives interest to this suggested process, but the temperature mentioned would alone be sufficient to produce a "reclaiming" effect, whilst the wide variety of tellurium compounds quoted, including hydrogen telluride, antimony telluride, and tellurium chloride, suggests that the nature of this additional ingredient is immaterial.

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[77] D. F. Twiss, *J.*, 1917, 786 and 787.

[78] *Ann. Repts.*, 1917, 350.

[79] B. J. F. Varenhorst and J. G. Fol, Ger. Pat. 302995; *J.*, 1918, 341A.

[80] Dunlop Rubber Co. and D. F. Twiss, Eng. Pat. 980, 1918.

[81] F. A. Fahrenwald, U.S. Pat., 1269168; *J.*, 1918, 596A.

Vulcanisation without Sulphur.

From its general analogy with sulphur, selenium might be expected to be capable of affecting rubber in a similar manner. Tests by R. Ditmar[82] in this direction had been discouraging, only colloidal solutions of selenium in rubber being obtained. C. R. Boggs[83] has now published results showing that it is indeed possible to vulcanise rubber by means of selenium, and that with the aid of β-naphthylamine as catalyst the period necessary for vulcanisation at 135° C. can be reduced to approximately twice that required for the corresponding sulphur mixing. In tensile strength and elongation the products are comparable with the analogous sulphur products, but show less tendency to deterioration when stored.

Ostromyslenski's method for the vulcanisation of rubber by means of organic nitro-compounds,[84] judging by published investigations, has hitherto received regrettably little attention from the point of view of the mechanical characteristics of the vulcanised products. The reference of H. P. Stevens[85] to this matter has now been considerably extended by E. Bunschoten,[86] who shows that nitrobenzene and *m*-dinitrobenzene alone do not vulcanise rubber; on the addition of certain metallic oxides, particularly lead oxide, vulcanisation occurs readily, but the usual organic vulcanisation catalysts are ineffective. *m*-Dinitrobenzene gives much better results than nitrobenzene, and it is interesting to note that different grades of rubber show variation in rate of vulcanisation by this new method. For a mixing of smoked sheet rubber 100, litharge 8, and *m*-dinitrobenzene 4, vulcanised at 147° C., the best physical properties are produced in 10 to 15 minutes; if the heating is unduly prolonged, marked deterioration is observed in the mechanical qualities, and even with a well vulcanised sample depreciation is rapid, the material becoming quite soft after a few weeks. Attempts to prepare hard rubber by prolonged treatment of raw rubber with dinitrobenzene and litharge were unsuccessful, a soft leathery mass being obtained on which an efflorescence of *m*-nitraniline gradually appeared. The formation of this substance is in agreement with Ostromyslenski's view that the effect of the nitro-compounds is due to an oxidising action, but no similar vulcanisation effect was observable in experiments with many inorganic oxidising agents. As the addition of *m*-dinitrobenzene to a benzene solution of rubber causes an increase in the viscosity, the suggestion is made that vulcanisation by organic nitro-compounds is to be ascribed to a polymerisation effect on the rubber.

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[82] *Sitzungsber. Akad. Wien*, 1905; *J. Chem. Soc.*, 1905, ii. 701.

[83] *J. Ind. Eng. Chem.*, 1918, **10**, 117; *J.*, 1918, 188A. U.S. Pat. 1249272; *J.*, 1918, 66A.

[84] *J.*, 1916, 159; *Ann. Repts.*, 1916, 212.

[85] *J.*, 1917, 107.

[86] *Chem. Weekblad*, 1918, **15**, 257; *J.*, 1918, 251A; *Kolloid Zeits.*, 1918, **23**, 25; *J.*, 1918, 664A.

Analysis.

Many papers during the year have touched on the extraction of rubber with acetone, an operation which is of prime importance in the examination both of raw and vulcanised material. The recent general shortage of this solvent has served to emphasise the absence of any satisfactory substitute for it in the determination of the proportion of "resins" in rubber, gutta, and balata.[87] The resinous constituents of raw rubber not only serve as a rough index of the quality of the rubber, a higher resin content being usually associated with a poorer grade, but the resins of *Hevea* rubber, wild or plantation, are inactive towards polarised light, and therefore are of assistance in distinguishing such rubber from most other grades of rubber, the resins of which exert a distinct dextro-rotation on the plane of polarisation.[88] These resins are only incompletely dissolved by caustic alkali solutions, the optical activity being confined to the unsaponifiable portion.

The percentage of natural resins remains almost unaltered during vulcanisation, although a very slight decrease may be observed. Where a large number of samples of vulcanised rubber-sulphur mixings have to be examined as to the proportion of sulphur remaining uncombined, it is therefore possible to obtain the desired results from a knowledge of the resin content of the original raw rubber and the amount of the acetone extract of the various samples.[49]

Atmospheric oxidation of raw or vulcanised rubber, which proceeds especially rapidly after removal of the natural resins, also gives rise to resinous products which are optically inactive and wholly saponifiable; this is well known to provide a possible source of error in the estimation of the amount of rubber substitutes of the "vulcanised oil" type in manufactured rubber goods; it may, however, also introduce a disturbing factor in the determination of "free sulphur." On numerous occasions experimental results have been reported in support of the claim that even after very prolonged extraction with acetone vulcanised rubber will still yield small quantities of sulphur to further extraction,[89] and such results have been adduced as evidence that the "combined" sulphur is not chemically combined, at any rate in its entirety. Unless the conditions of the experiment in such investigations are such as to preclude absolutely the possibility of oxidation during the prolonged extractive treatment, further evidence is necessary before the results can be unreservedly accepted.

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[87] P. Dekker, *Gummi Zeit.*, 1917, 31, 824; *J.*, 1918, 341A; A. van Rossem, *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1917, 2, 46; *J.*, 1917, 1104.

[88] Hinrichsen and Marcusson, *Z. angew. Chem.*, 1910, 23, 49; *J.*, 1910, 224; A. van Rossem, *Comm. Netherland Govt. Inst. for advising Rubber Trade*, 1917, 2, 49.

[89] C. D. Harries, *Ber.*, 1916, **49**, 1196: C. D. Harries and E. Fonrobert, *ibid.*, **49**, 1390; *J.*, 1916, 747, 1027.

ACIDS, ALKALIS, SALTS, ETC.

By H. A. Auden, M.Sc., D.Sc.,

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A general survey of the published results of work included in this section has not revealed anything of a sensational character. Certain tendencies are perceptible, such as the greater appreciation and practical application of the results of research in physical chemistry to manufacturing problems. An example of this is found in the relatively large number of references to processes for the separation of soluble salts. The commercial application of the phase rule to this class of problem is becoming more apparent, though it is naturally the recognition and not the procedure which is notable. In many factories due appreciation of research work is still lacking, as the application of the results is not always obvious to the non-chemical mind. There is apparently an increased interest in the utilisation of the resources of the Empire, stimulated undoubtedly by the shortage of some imported materials. The creation of the Mineral Resources Bureau and other Committees for Research is a good augury for the future, provided that these departments are not confined to a group of officials who may rapidly lose touch with the requirements of manufacturers. Another tendency is the beginning of a wider appreciation of the importance of chemical manufacture from the standpoint of the political economist. It is to be hoped that the impetus given to this aspect by the war will not wane when this stimulus is withdrawn. Several articles have appeared which support this view. "The Mineral Wealth of Spitzbergen,"[1] and P. Kestner's "The Alsace Potash Deposits"[2] may serve as striking illustrations. A competent chemically minded economist who could survey the subject from a broad standpoint has, so far as we are aware, not yet emerged. A work "isomorphic" with Buckle's "History of Civilisation" might be written, avoiding some of the pitfalls revealed by the writings of that industrious author. The greatest number of references encountered in the chemical journals is in the group relating to potash recovery, though descriptions and suggestions relating to the production of nitrogen compounds are not far behind.

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[1] *J.*, 1918, 239R.

[2] *J.*, 1918, 291T.

The Chief Inspector of Works under the Alkali Acts reports[3] an aggregate of 1582 works, in many of which more than one registered process was carried on in 1917. The opinion is expressed that there appears to be a considerable increase in the numbers of those who recognise the advantages to be derived from the most efficient works control, and the provision of properly staffed laboratories for research. "There is still in many cases, instead of a proper appreciation of the collateral advantages which are secured by efficient control, a feeling that low expenditure on management is one step towards reduced cost of production. That this is an erroneous view has been repeatedly proved."

The pre-war consumption of pyrites in the United States[4] was about 900,000 tons, mostly from Spain, but some from Newfoundland. Since the war Canada has supplied 250/300,000 tons. About 800,000 tons of sulphur was also used, about half of this being from Sicilian mines. Considerable deposits of sulphur occur in New Zealand, but difficulties, mainly those of transport, were not overcome and the mines were abandoned. If the obstacles could be surmounted, Australian imports, amounting to 20,000 tons, might be obtained from this source, and the requirements of New Zealand herself might be met from her own mines instead of by importation from Japan as at present. Owing to the insufficiency of supplies of Spanish pyrites five mines in the southern States of America have been started,[5] yielding 400 tons per day, to increase to 1000 tons in a month or so if required. According to calculation, Spain[6] still possesses 250,000,000 tons of ore; the annual normal output is about 3,000,000 tons. Some of the sulphur mines using the Frasch process are reported[7] to have yielded over 100,000 tons of sulphur, two mines alone producing 99% of the total. The pyrites raised in 1917 was 462,660 tons, being nearly 40,000 tons more than in the previous year. The production of sulphuric acid is stated to have been above 7,000,000 tons from 483,827 tons of sulphur, 1,257,138 tons of pyrites, 17,380 of pyrites containing gold, silver, and lead, 856,033 tons of copper pyrites, and 736,911 tons of zinc blende.

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[3] *Chem. Trade J.*, 1918, **63**, 19; *J.*, 1918, 306R.

[4] *Statist*, Dec. 29, 1917; *J.*, 1918, 12R.

[5] *J.*, 1918, 76R.

[6] *U.S. Comm. Rep.*, June 19, 1918; *J.*, 1918, 342R.

[7] *U.S. Geol. Survey*, July 1918; *J.*, 1918, 381R.

The Grong sulphur ore deposits[8] recently purchased by the Norwegian Government are stated to contain 6,500,000 tons of 44/45% sulphur, 1,000,000 tons of 50/51%, and 1,200,000 tons of 42% with 2·2% copper. An annual export of about 400,000 tons is expected. The number of chemical works in Germany is given[9] as 14,903 in 1916 compared with 14,914 in 1915.

Japan[10] shows important development in the manufacture of dyes and of sodium and nitrogen products. Marked increases have been made in drugs and celluloid, but the greatest progress has been made in potassium chlorate, phosphorus, caustic soda, and bleaching powder. The total of chemical products manufactured is 630,000 tons per annum, expected to rise shortly by a further 20,000 tons.

J. N. Friend[11] gives some useful hints on painting of structural work. As a result of trials and scientific deductions he concludes that successive thin coats of a finely ground black or red paint applied to the surface, with the loose scale only removed by scraping, give the best results. This, surely, is not intended to apply to the situations encountered by the works chemist.

The use of the Cottrell types of precipitators is extending, and has in most cases been found very efficient. The " plate " type is generally preferable for dusty gases and the " chain " type for mists. In one case quoted by J. N. Carothers,[12] complete precipitation of suspended matter in large volumes of gas at a velocity of 3 ft. per second at a temperature of 300° C. was achieved. A full account of the applications of the Cottrell apparatus is given in an article by H. J. Bush.[13]

SULPHURIC ACID.

G. L. Moss[14] contrasts the working of the older systems of sulphuric acid manufacture with those of recent introduction. Amongst other features, mention is made of the use of a wash tower introduced before the Glover tower, with a view to confining the contamination of the acid by dust to 3–5% of the make. The gases leaving the wash tower are filtered through coke, and reheated by a separate heater. The Opl system working with 2 ft. chamber space is described as ideal, but much power is required for pumping, and the process is in practice still experimental. Loss of nitre, when it sets in, occurs with great rapidity and unremitting scientific supervision is necessary. There is very little to be said in favour of using nitric acid on the towers —this, except in emergency, being an intolerable nuisance. A better procedure is to bring up Gay-Lussac acid to the standard figure with nitric acid. Another attempt to remove dust from burner gases is that of E. L. Wilke,[15] who passes the gas tangentially into an outer annular chamber at about the middle. This causes the dust to separate from the gas, which then flows to the inner chamber, containing heated contact material, through a number of passages connecting the upper end of the outer and the lower end of the inner chambers.

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[8] *Chem. Trade J.*, 1918, **63**, 183; *J.*, 1918, 418R.

[9] *Chem.-Zeit.*, 1917, 747; *J.*, 1918, 13R.

[10] *The Internat. Trade*, Oct. 1917; *J.*, 1918, 13R.

[11] *Iron and Steel Inst.*, *Carnegie Schol. Mem.*, 1918, **9**, 1; *J.*, 1918, 736A.

[12] *J. Ind. Eng. Chem.*, 1918, **10**, 35; *J.*, 1918, 87A.

[13] *J.*, 1918, 389R.

[14] *J.*, 1918, 68T.

J. Thede[16] contributes interesting points arising in the practice of the intensive system of sulphuric acid manufacture. A largely increased circulation of nitrous compounds is essential and consequently special arrangements are necessary. Petersen's regulator[17] has given good results. Meyer's process, using tangential inlets to circular chambers, promotes the formation of acid. An essential feature is high chambers, about 10–15 metres in height. An example of increased output without special devices is described. The amount of circulating acid was increased greatly beyond the usual 2–4 times the "make." The burner gases were driven by a wrought iron fan to the Glover tower at a temperature of about 500° C., and a second fan of hard lead was installed between the first and second Gay-Lussac.

L. B. Skinner[18] notes some of the methods adopted to increase the output of acid in the United States. Addition of brimstone to Hegeler blende furnaces resulted in an increase of chamber output by 20%. Australian concentrates were used and will probably be continued after the war conditions have ceased. The lead towers are being displaced by cheaper masonry designs and stoneware fittings are giving place to ferrosilicon castings.

The Tennessee Copper Co.'s acid plant, producing 300 tons of 60° B. acid daily, is described by A. M. Fairlie.[19] Two plants are employed, one of about 4,000,000 cubic feet divided between thirty-four chambers, the other of four large chambers with about 2,250,000 cubic feet. The sulphur dioxide content in the blast-furnace gases is 3–6%.

The concentration of sulphuric acid is still the subject of investigation. P. Pipereaut and Helbronner[20] overcome the comminution of the acid and the formation of anhydride, which is a usual feature of plants involving the passing of acid and flue gases in countercurrent, by allowing the acid to flow undisturbed through shallow vessels in the same direction as the flue gases. Each vessel is a rectangular box (1 × 1·5 × 0·5 m.) with the outlet at a lower level than the inlet. By adjusting the proportions of hot gas at 1200° C. and 53° B. acid so that (*a*) the acid is not heated above 300° C. (at which temperature anhydride formation begins, and (*b*) the gases leaving the system are still considerably below the point of saturation with water vapour, low fuel consumption, reduced atmospheric pollution through low escape, and less wear and tear of plant are claimed.

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[15] U.S. Pat. 1270997; *J.*, 1918, 579A.

[16] *Z. angew. Chem.*, 1918, **31**, 2; *J.*, 1918, 464A.

[17] *J.*, 1910, 1250.

[18] *Met. and Chem. Eng.*, 1918, **18**, 82; *J.*, 1918, 147A.

[19] *Met. and Chem. Eng.*, 1918, **19**, 404; *J.*, 1918, 652A.

[20] *Monit. Scient.*, 1917, **61**, 265; *J.*, 1918, 6A.

In a description of the iron oxide contact process followed by platinum contact, attention is drawn by H. Ditz and F. Kanhäuser[21] to the volatility of lead sulphate, especially in the presence of selenium. The presence of selenium has probably a deleterious effect on the oxidation of sulphur dioxide. The process should convert 95% of the sulphur burned, but more usually the conversion is only about 92%. The plant studied showed occasionally a yield below 90%, which may be due to the toxic action of arsenic on the platinum and probably selenium and lead on the iron oxide. According to Szigeti,[22] tantalum can replace platinum in chamber sprays; the plates have shown great durability in practice.

References have been made in former volumes to the establishment of works in Germany for the production of sulphuric acid from gypsum and clay. The sulphur dioxide obtained is converted catalytically and the residue is used for cement. The suggestion is made[23] that there are several sources of waste material rich in calcium sulphate, but which cannot be used for plaster. The old and broken moulds of potteries might thus be utilised; at present these are a source of expense and inconvenience.

A very interesting study, resulting in the separation of a fairly concentrated acid from nitre cake and gypsum, is embodied in a patent taken out by F. A. Freeth.[24] The nitre cake, calcium sulphate, and water are mixed in the proportions 689 : 180 : 313 and heated to 50° C., with constant stirring, till the solution is saturated with sodium bisulphate and calcium sulphate. The sodium calcium double salt separates out, and is removed with some calcium sulphate. The solution is cooled to 25° C. till the bisulphate has separated, this is removed, and the solution is evaporated until it contains 70–75%

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[21] *Z. angew. Chem.*, 1918, **31**, 149, 153; *J.*, 1918, 577A.

[22] *Chem.-Zeit.*, 1918, **42**, 115; *J.*, 1918, 333A.

[23] *J.*, 1918, 378R.

[24] Eng. Pat. 117649; *J.*, 1918, 578A.

of sulphuric acid; on cooling again to 25° C. the double salt $Na_2SO_4.3H_2SO_4,2H_2O$ separates. On the removal of this double salt the solution contains 75–80% of H_2SO_4 and less than 1% of sodium sulphate. The mixture of sodium bisulphate and the polysulphate is treated with more calcium sulphate and the cycle repeated. The double sodium calcium sulphate is decomposed by extraction with hot water. Temperatures higher or lower than 50° C. are unfavourable.

An outline of various methods of dearsenication of sulphuric acid is given by H. E. J. Cory.[25] Some useful thermal data[26] relating to sulphuric acid and oleum and graphs[27] for mixing oleum have been recently published. An outlet for non-cupreous pyrites cinders[28] is reported, and it appears hopeful that plants designed to deal with 300,000 tons will shortly be ready.

SULPHUR CHLORIDES.

A short account of the manufacture of mono- and tetra-chloride of sulphur has been published.[29] We cannot agree with the tone of the description as the preparation of these substances is very far from easy, and "pure" products are extremely rare.

HYDROCHLORIC ACID.

B. Lepsius[30] has considered the possibilities of utilising the waste liquors, rich in magnesium chloride, which are produced in large quantities in the potash industry.[31] The liquors are evaporated to one-third, mixed with 15% of magnesium oxide, and the mass allowed to set. By calcination in a rotary tube at 600° C., crude magnesium oxide and hydrochloric acid are obtained. The outlook for the sale of the acid is not so favourable from the commercial aspect as that of the magnesia. A large expansion of the use of magnesium oxychloride for cement would be favourable, but as it is not weatherproof it is unlikely to become sufficiently general.

The conversion of chlorine to hydrochloric acid, a proceeding likely to be made more use of in the future, is the subject of an addition

[25] *Chem. Trade J.*, 1918, **62**, 89; *J.*, 1918, 122A.

[26] A. W. Porter, Faraday Soc., Dec. 12, 1917; *J.*, 1918, 27A.

[27] E. C. Craven, *Chem. News*, 1918, **117**, 217; *J.*, 1918, 412A.

[28] *Bd. of Trade J.*, Oct. 3, 1918; *J.*, 1918, 395R.

[29] *Chem. Trade J.*, 1918, **62**, 508.

[30] *Z. angew. Chem.*, 1918, **31**, 93; *J.*, 1918, 368A.

[31] Ger. Pat. 278106; *J.*, 1915, 227.

to a previous patent of C. W. Baumann.[32] Hydrochloric acid gas is added to the mixture of the chlorine and hydrogen in the explosion chamber to prevent overheating and to make the process continuous.

NITRE CAKE, SULPHATES, ETC.

In October 1918 sulphuric acid was being produced at the rate of about 1,800,000 tons per annum.[33] Much economy has been effected by the use of nitre cake, produced at the rate of about 28,000 tons per month, of which 23,000 tons per month is utilised in twenty-five different trades. Nitre cake is reported to be successful in Canadian paper mills.[34] An account of the rational use of this by-product,[35] containing useful suggestions, may be referred to by those interested.

J. Grossmann[36] has made further suggestions which are embodied in patents. A mixture of finely ground nitre cake and sodium nitrate is heated on trays carried on trolleys through a decomposing chamber, the temperature rising from 150° C. at one end to 250° C. at the other. Air may be excluded or introduced according to the products required. To assist grinding,[37] a mixture of nitre cake with 27% of sulphuric acid at a temperature of 50° C. is recommended. The optimum temperature for grinding varies with the percentage of free acid. The suggestion has been made[38] to produce sodium sulphide by the reaction of nitre cake with iron oxide and reduction with carbon. We understand that sodium sulphide has been produced for a considerable period by a more direct method than this. Other suggestions are the preparation of magnesium sulphate from dolomite or magnesite and separation by fractional crystallisation. The use of nitre cake for making carbon dioxide has been patented by W. T. Mackey and J. S. Carrol.[39]

The phases and solubilities relative to mixtures of sodium and ammonium sulphates are given by C. Matignon and F. Meyer.[40] The separation of the mixed sulphates of sodium and ammonium by controlled concentration and crystallisation is the subject of a patent by H. M. Dawson.[41] Pure ammonium sulphate separates out at

[32] Ger. Pats. 301903 and 305306; *J.*, 1918, 414A.
[33] *J.*, 1918, 395R.
[34] *J.*, 1918, 319R.
[35] *J.*, 1918, 104T.
[36] Eng. Pat. 114180; *J.*, 1918, 214A.
[37] Eng. Pat. 115340; *J.*, 1918, 370A.
[38] *Chem. Trade J.*, 1917, **61**, 528.
[39] Eng. Pat. 109511; *J.*, 1917, 1128.
[40] *Comptes rend.*, 1917, **165**, 787; *J.*, 1918, 29A.
[41] Eng. Pat. 114236; *J.*, 1918, 241A.

100° C. from the mother liquor remaining after considerable separation of sodium sulphate by previous evaporation and cooling, so long as the molecular ratio $(NH_4)_2SO_4 : Na_2SO_4$ in the hot mother liquor does not fall below 2·7. The reaction between finely powdered soda crystals and ammonium sulphate has also been studied.[42] At temperatures between 59·3° C. and −16° C.

$$Na_2SO_4,10H_2O + (NH_4)_2SO_4 = Na_2SO_4(NH_4)_2SO_4,4H_2O + 6H_2O$$

takes place; above 59·3° C. the double salt decomposes with the formation of anhydrous simple salts. The ternary system has been determined at temperatures between the eutectic temperature, − 19·5° C., and 100° C. At 26·5° C. the Glauber salt is transformed into anhydrous sodium sulphate in the presence of the double salt.

A method of preparing ammonium sulphate by means of nitre cake is described[43] and possesses some interest. The nitre cake is neutralised with ammonia and an excess depending on the percentage of sodium sulphate is added. The mixture is heated and treated with carbon dioxide under pressure, producing in the first place ammonium bicarbonate, and further ammonium sulphate and sodium bicarbonate. The mother liquors after treatment with more nitre cake are fractionally crystallised to separate the sulphates, the sodium sulphate being used in a fresh charge.

P. Parrish[44] describes the procedure adopted by the Stafford Gas Works to produce saleable mixed sodium and ammonium sulphates. Nitre cake, finely ground, is added to the acid charge pots, in such a manner that the acidity does not fall below 6%. The presence of nitrate is objectionable on account of the corrosion of the lead. As an alternative the nitre cake may be added to the feed acid. At the Llwynpia works, nitre cake solution of 6% acidity is fed along with the free acid in certain proportions. When separation of crystals occurs, some liquor is run off and cooled to 46° C., causing most of the sodium sulphate to crystallise out. The mother liquor is returned to the saturator. Ammonium sulphate with a 23·8% ammonia content is obtained as the final product. At Langwith a trial on a Mond recovery plant was made, in which the cooled gases, freed from tar, were scrubbed in a tower fed with 3–4% sulphuric acid. On reaching the saturation point, the solution was evaporated. The mother liquor from the sulphate crystals, maintained at about 80° C., was used to wash the nitre cake so that very little sodium sulphate passed into solution. The liquor was used again in the tower after dilution with washings from the sodium sulphate *sludge. A salt of* 24·5% ammonia content was produced.

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[42] *Chem. Soc. Trans.*, 1918, **113**, 675; *J.*, 1918, 577A.

[43] Soc. Indus. Prod. Chim., Eng. Pat. 109814; *J.*, 1918, 545A.

[44] *Gas J.*, 1918, **143**, 395; *J.*, 1918, 577A.

E. Hart[45] separates sodium sulphate as a granular mass by blowing cooled air into an aqueous solution of nitre cake of sp. gr. 1·30 at a temperature of — 40° C. W. C. Blasdale[46] has studied the conditions governing the fractional separation of potassium and sodium salts. The investigation is accompanied by phase diagrams. The equilibrium of

$$3KCl + 2Na_2SO_4,10H_2O \rightleftarrows K_3Na(SO_4)_2 + 3NaCl + 20H_2O$$

was studied for 0°, 25°, 50°, 75°, and 100° C. The application of the results described affords the most efficient separation of potassium salts from the ash of kelp or from brines.

AMMONIA.

An interesting article by P. Parrish[47] describes the means employed to desulphurise and decarbonate crude liquor in the manufacture of ammonia, special attention being given to the prevention of losses and the avoidance of blockages. G. A. Hebden[48] gives a very full account of the production of pure liquor ammonia and indicates the essentials of a plant, dealing with 400 tons of crude liquor per day, for the removal of carbonate, hydrogen sulphide, pyridine, phenols, &c. The supply of ammonia freed from the impurities mentioned above has an important bearing on the production of nitric acid, in consequence of the marked deleterious effect on the platinum nets. The numerous causes of loss of ammonia in the manufacture of concentrated ammonia are summarised by A. Marsden.[49] The transformation of plant for ammonium sulphate to that for the production of concentrated liquor is described by W. Greaves.[50] This alteration of plant has been a matter of importance during the last two years owing to the necessities of war. In the case in question the incoming liquor contained 0·75% of ammonia and 0·23% of hydrogen sulphide, and yielded a finished product containing 28–29% of ammonia and 0·20% of hydrogen sulphide.

[45] U.S. Pat. 1258895; *J.*, 1918, 302A.

[46] *J. Ind. Eng. Chem.*, 1918, **10**, 344; *J.*, 1918, 369A.

[47] *Gas J.*, 1917, **140**, 554; *J.*, 1918, 28A.

[48] *Gas J.*, 1917, **140**, 609; *J.*, 1918, 28A.

[49] *Gas J.*, 1917, **140**, 412, 554, 609; **141**, 398; *J.*, 1918, 231T.

[50] *Gas J.*, 1918, **141**, 398; *J.*, 1918, 179A.

E. V. Evans and the South Metropolitan Gas Co.[51] have patented a procedure leading to the production of a white and neutral ammonium sulphate. The ammonia is added to hot sulphuric acid of such dilution that no crystals separate until the solution is slightly alkaline. The liquid is filtered and cooled, and the salt allowed to crystallise.

AMMONIA OXIDATION AND NITRIC ACID.

G. B. Taylor and J. D. Davis[52] give useful information on the analytical control of the ammonia oxidation process. The efficiency of the converter depends on the establishment of conditions favourable to the reaction $4NH_3 + 5O_2 = 4NO + 6H_2O$ and unfavourable to $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. A contribution by W. G. Adam[53] gives some account of the initial work done on the problem. Wilton and Davis in 1908 achieved successful oxidation of ammonia on a works and laboratory scale, but until 1917 the relative prices of ammonia and sodium nitrate hindered commercial application for the production of nitric acid. Since 1917 several sulphuric acid plants have used ammonia oxidation in place of "potting" nitre. If the oxidation is not complete free nitrogen will result, as indicated in the equations given above. A minimum time of contact is necessary, this is calculated for a 1 : 10 ammonia-air mixture to be about 0·0046 sec. at 600° C.

Further experimental data are given by G. B. Taylor, J. H. Capps, and A. S. Coolidge.[54] In those relating to the most suitable conditions for absorption of the products of the oxidation in water, it was found that this should be carried out at as low a temperature as possible. It was also found conducive to good working not to allow the oxygen in the exit to fall below 5%. Some acid is lost through the non-absorption of acid mist, but by means of a small Cottrell precipitator this was much reduced. The controlling reaction in this process is $2NO + O \rightleftarrows 2NO_2$ which requires the provision of both time and space. Taylor and Capps[55] have shown that 0·02% of acetylene reduces the yield of nitric acid from 95% to 89%, and 0·1% brings it down to 65%.

J. R. Partington[56] records the results of investigations and experiences with one form of convertor which is illustrated. A purified 25% ammonia liquor is the source of the ammonia, which is filtered, mainly with the object of removing any oxide of iron, before passing over the 80-mesh platinum gauze. $4NH_3 + 5O_2 = 4NO + 6H_2O + 220$ kg. cal. represents the action, which is initiated by a non-luminous flame or by electric heating. Under established conditions 1·5 tons of nitric acid per square foot per 24 hours is produced with a 95% efficiency, or about 85% without an external source of heat. Plants are in use in England, France, Italy, and Russia, and the United States have allocated £20,000,000 for the erection of five large plants for the production of nitric acid from ammonia.

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[51] Eng. Pat. 111309; *J.*, 1918, 30A.

[52] *J. Ind. Eng. Chem.*, 1917, **9**, 1106; *J.*, 1917, 1005; 1918, 54A.

[53] *Chem. Trade J.*, 1918, **62**, 181; *J.*, 1918, 179A.

[54] *J. Ind. Eng. Chem.*, 1918, **10**, 270; *J.*, 1918, 298A.

[55] *J. Ind. Eng. Chem.*, 1918, **10**, 457; *J.*, 1918, 465A.

[56] *J.*, 1918, 337R.

A. A. Wells and the Ellis Foster Co.[57] pass the ammonia gas through a heated chamber with the interior surfaces covered with an oxidising catalyst.

The plentiful water power of Switzerland, and the fact that practically no imported material is required cause P. A. Guye[58] to conclude that the arc process of nitric acid manufacture is the most suitable to supply the annual requirements of 5000 tons of nitric acid and 5000 tons of nitrogenous fertilisers. In order to avoid the transport of nitric acid the production of liquid nitrogen peroxide (boiling point 26° C.) is suggested; as the liquid does not attack sheet iron the suggestion may be feasible. The 800 tons of ammonia which Switzerland requires could be obtained by the reduction of nitric acid by hydrogen in the presence of nickel at 250°–300° C. giving a 70% yield. An article[59] by the same author and another rather throws doubt on the commercial advantages of the reduction of nitrogen oxides to ammonia.

E. Bergve and the Norsk Hydro-elekt. Kvaelstof Co.[60] obtain a highly concentrated nitric acid by causing a mixture of nitrogen peroxide, oxygen, and water (or weak nitric acid) to react under a pressure of twenty atmospheres at a temperature of 70° C. The same company[61] has made an addition to a previous patent[62] and now suggests that for drying moist nitric acid vapour[63] 80% sulphuric acid, at a temperature of 30° C., be introduced at the top of the tower and steam so regulated that the nitric acid leaves the tower as vapour at about 95° C.

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[57] U.S. Pat. 1252976; *J.*, 1918, 148A.

[58] *Schweiz. Chem. Zeit.*, 1918, **2**, 3; *J.*, 1918, 179A.

[59] *Helv. Chim. Acta*, 1918, **1**, 33; *J.*, 1918, 412A.

[60] U.S. Pat. 1273991; *J.*, 1918, 622A.

[61] Ger. Pat. 305915; *J.*, 1918, 466A.

[62] Ger. Pat. 278867.

[63] Fr. Pat. 465504; *J.*, 1914, 643.

At the inaugural meeting of the Société de Chimie Industrielle, Prof. Haller[64] reviewed the course of events leading to the development of the Haber process. He points out that probably the validity of the Badische patents is seriously compromised by previous specifications. The process appears to be epitomised by a series of patents granted to Tellier and Dufresne,[65] Tessié du Motay,[66] Nitrogen Co. of Paris and Tellier,[67] Hlavati,[68] Minekompani of Christiania,[69] and Chatelier.[70] E. B. Maxted[71] in his notes on the catalysis and thermal synthesis of ammonia shows that the highest possible yield for a catalytic chamber of given size is obtained with very high speed of circulation and with the minimum value for the percentage of ammonia formed per passage, but that these conditions are not necessarily the most economical. Further advantages are gained by high pressures, 180 atmospheres being practicable. The influence of temperature has also been investigated.

The *Neue Zürcher Zeitung*[72] reports a process for obtaining nitrogen from air, working at four times the velocity and resulting in a yield 80% greater than the old method. The Elektrizitätswerk Lonza[73] suggests the removal of oxygen from air by passing it through ammonium sulphite at a temperature of 70°–75° C. until the oxygen content is reduced to 0·1–0·2%; the nitrogen may then be used for the production of cyanamide.

POTASH.

The number of articles and patents which deal with the production of potassium salts still continues to be large. Owing to the absence of potash from the large well-known deposits the investigations relate for the most part to methods of production from other sources which for convenience are here classified as in 1917 under the following headings: (1) Rocks such as felspars, leucites, alunite, greensands. (2) Lake waters and lacustrine deposits, sea-water, and waste lyes. (3) Blast-furnace and cement flue-dusts. The output[74] of all potash materials produced in the United States in 1917 was 126,577 short tons, containing an average of 26·4% K_2O, and was about three times that of 1916. Brines, including those from Searles Lake, contributed about 45%, kelp and alunite 10%, molasses residues 9%. The recovery from cement dusts is being rapidly extended, and it is expected that the production from this source may take the second place in the summary of 1918. The recovery from blast furnaces may eventually be large when those who operate steel plants are enabled to work under less trying conditions.

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[64] *Chem. Trade J.*, 1918, **62**, 413.

[65] Eng. Pat. 1833 (1865).

[66] Fr. Pats. 92346 (1871); 138472 (1881).

[67] Ger. Pat. 17070 (1881).

[68] Aus. Pat. 45/2938 (1895).

[69] Fr. Pat. 255183.

[70] Fr. Pat. 313950 (1901).

[71] *J.*, 1918, 232T.

[72] *J.*, 1918, 262R.

[73] Ger. Pat. 302679; *J.*, 1918, 335A.

[74] *U.S. Geol. Survey Press Bull.*, May 1918; *J.*, 1918, 264R.

The general surveys of the whole potash problem to which special attention is drawn are those of P. Kestner,[75] dealing mainly with the Alsatian deposits, K. M. Chance,[76] "Prospects of founding a potash industry in England," and L. Bradley,[77] in which the question of recovery of potash as a by-product in the iron and cement industries is reviewed. The use of silicates containing potash in the manufacture of cements is discussed. It has long been in the mind of the writer of these reports that should the production of a cement with a more pleasing surface finish and tone result from the use of felspars, this fact alone would enhance the value of the process as a cement proposition. E. A. Ashcroft [78] states that if felspar containing 10% of potash, ground to pass a 100-mesh sieve, be heated, in the absence of air and moisture, with its own weight of salt for 2 hours to a temperature of 900°–1000° C., 85% of the potash is rendered soluble, without loss by volatilisation. The reaction is stated to be a reversible one:

$$2NaCl + K_2O.Al_2O_3.6SiO_2 \rightleftarrows Na_2O.Al_2O_3.6SiO_2 + 2KCl.$$

The products are an insoluble albite and a mixture of sodium and potassium chlorides. The discovery is due to Bassett,[79] but the problem has been independently and exhaustively studied by Ashcroft, who has patented [80] the process, including the production of caustic potash from the reaction product. S. R. Scholes [81] fuses the felspar with anhydrous potassium or sodium carbonate to supply one equivalent to every two of silica. The mass is poured into water and ground, boiled with water, and carbon dioxide passed in till the maximum of dissolved alkali is reached. Part of the evaporated product may be used for treating further quantities of felspar, and the cycle repeated, thus producing liquors of increasing potash content; alternatively the product may be evaporated to the point at which most of the sodium carbonate crystallises out, the solution evaporated to dryness, and the residue used as above. The quantity of mixed carbonates removed at each cycle is equal to the amount of potassium carbonate extracted from the rock. B. F. Halvorsen [82] combines the extraction of potash salts with the production of ammonia by heating felspar and cyanamide to 650° C. with superheated steam. The addition of salts such as chlorides, sulphates, or nitrates facilitate the reaction. After removal of the ammonia, the filtered solution is neutralised with acid to precipitate the alumina, again filtered, evaporated, and crystallised. H. W. Charlton [83] digests finely ground greensand with lime and water at 225 lb. pressure for 2–4 hours. The filtrate contains fairly pure potassium hydroxide; the residue may be used for making bricks and tiles. This method is considered more advantageous than that employing felspar, as it avoids the troublesome separation of the sodium hydroxide and alumina. One ton of greensand is capable of producing about 100 lb. of K_2O and cement for 20/30,000 bricks. The Australian Advisory Council of Science and Industry [84] have investigated various alunites as sources of potash.

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[75] *J.*, 1918, 291T.

[76] *J.*, 1918, 222T.

[77] *Chem. and Met. Eng.*, 1918, **19**, 457; *J.*, 1918, 653A.

[78] Inst. Min. and Met., Dec. 20, 1917; *J.*, 1918, 54A.

[79] U.S. Pat. 1095306.

[80] Eng. Pat. 114743; *J.*, 1918, 301A. Eng. Pat. 113211; *J.*, 1918, 180A.

[81] Eng. Pat. 117755; *J.*, 1918, 579A.

E. E. Thum [85] gives a detailed account of the Nebraska potash industry, which is reported to be producing salts with a 25% potash content at the rate of 32,000 tons K_2O per year. A deposit [86] containing the sulphates of potassium, sodium, and magnesium occurs in a dried-up lake about thirty miles north of Maple Creek, Saskatchewan. The area of the lake bed is 2¼ × 1 mile and a railway is planned from Maple Creek to permit of work beginning at once. The Pintados Salar in N. Chili is described by H. S. Gale [87] as being about twenty square miles in extent and containing 3–7% potash as glaserite. Wells gives a laboratory method of extracting the potash salts. J. H. Hildebrand [88] recommends a method based on van't Hoff's studies of oceanic deposits to recover potassium chloride from the sea-water of San Francisco bay.

C. M. Barton [89] of the Dupont Nitrate Co. gives an account of the extraction of potassium nitrate from "caliche" containing about 5%. The company produce 10,000 tons of 25% nitrate annually, and if all producers followed their lead 240,000 tons could be secured. He regards the production from cement dusts as a permanent one as, although the initial costs of precipitators, &c., are high, the running costs are low.

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[82] Eng. Pat. 107012; *J.*, 1918, 414A.

[83] *J. Ind. Eng. Chem.*, 1918, **10**, 6; *J.*, 1918, 87A.

[84] *Bull.* 3; *J.*, 1918, 239A.

[85] *Met. and Chem. Eng.*, 1917, **17**, 693; *J.*, 1917, 595; 1918, 87A.

[86] *J.*, 1918, 378R.

[87] *Eng. and Min. J.*, 1918, **105**, 674; *J.*, 1918, 298A.

[88] *J. Ind. Eng. Chem.*, 1918, **10**, 96; *J.*, 1918, 180A.

[89] *J.*, 1918, 135R.

The idea of raising the field fern on waste lands and extracting the potash (20%) from the ashes has been suggested.

K. M. Chance[90] points out that normally 15–20 tons of K_2O is contained in the burden charged to blast furnaces to produce 1000 tons of pig iron. Thus 200,000 tons is fed annually of which 50,000 tons is carried in blast furnace gas. The addition of salt increases the output without apparent detriment to the linings. The author regards the commercial aspects of the industry as favourable. The Ebbw Vale Steel and Coal Co.[91] have installed a Halberg-Beth cleaner, and plant for the extraction and concentration of potassium compounds is contemplated. Prof. R. A. Berry and D. N. McArthur[92] give a very full account of the recovery of potash from blast furnace gas and a good bibliography. The Stafford Coal Co. and J. R. Richmond[93] describe the procedure of extracting the potash salts as high-grade material from blast furnace flue dust, and note that the ammonia may also be recovered. A. R. Merz[94] is of the opinion that the water-soluble portion of cement mill dust differs with the fuel used, that from oil-fired kilns being higher than that from coal-fired kilns. This view is disputed by N. S. Potter and R. D. Cheesman.[95]

C. A. Higgins[96] shows the possibility of the production of acetone, acetone oils, ethyl esters, potassium chloride, and iodine from kelp by a fermentation process. Algin is also produced and may find extensive uses in future as substitute for gelatin and vegetable gum. More than half the 25 tons of 80% potassium chloride produced daily from kelp in the United States is obtained as 95% salt by the fermentation process.

E. Belloni[97] causticises potassium carbonate by lime with good agitation, excess of lime being avoided. The reaction is accelerated by increased pressure. The concentration should not exceed 12% of potassium carbonate. Losses are not caused by the formation of the double carbonates of calcium and potassium but by the excess of lime mechanically retaining the potash. The temperature, which does not affect the conditions of equilibrium in solutions of medium concentration, is preferably about 100° C., the volume being kept constant.

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[90] Cleveland Inst. Eng., Jan. 15, 1918. *J.*, 1917, 1006; 1918, 87A. Also Eng. Pat. 112338; *J.*, 1918, 88A.

[91] *J.*, 1918, 12R.

[92] *J.*, 1918, 1T.

[93] Eng. Pat. 117991; *J.*, 1918, 580A.

[94] *J. Ind. Eng. Chem.*, 1918, **10**, 106; *J.*, 1918, 180A.

[95] *J. Ind. Eng. Chem.*, 1918, **10**, 109; *J.*, 1918, 180A.

[96] *Chem. and Met. Eng.*, 1918, **19**, 432; *J.*, 1918, 653A.

[97] *Annali Chim. Appl.*, 1918, **9**, 115; *J.*, 1918, 368A.

SODA, LIME, AND MAGNESIA.

A report by the Canadian Pulp and Paper Association[98] deals with four modes of procedure for causticising sodium carbonate liquors and separation of the sludge. The use of filter presses affords great saving of space and labour. A. Zimmerman and L. M. Palmer[99] give a description of a continuous lime-slaking device, consisting of a series of cylinders maintained at the proper slaking temperature by external heating. A counter-current of air ensures the drying of the product before it is discharged.

The changes which lime undergoes during storage have been investigated by S. A. Woodhead.[100] Powdered lime, kept in a dry shed and turned frequently, was converted to the extent of 43% in sixty-four days into carbonate; the same lime heaped outside and exposed to the air for four months was converted only to the extent of 12%. Lump lime in bags, protected from the rain, lost 38% of its oxide in four months, and 52% when exposed to the air for the same period.

Several methods of separation of the constituents of dolomite have been published. H. A. Galt and The Columbia Chemical Co.[101] causticise sodium carbonate with calcined dolomite and treat the product with water and carbon dioxide under pressure. The magnesium carbonate in the filtrate is re-precipitated by boiling and converted into magnesium chloride by means of by-product calcium chloride. A. M. Mitchell[102] makes use of the conversion of calcium carbonate in dolomite to the crystalline state at about 540° C.; it is claimed that these crystals are readily separated from the magnesium oxide which is formed. The rate of hydration of magnesium oxide after ignition at various temperatures has been investigated by E. D. Campbell.[103] One sample obtained by the ignition of magnesite at

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[98] *Met. and Chem. Eng.*, 1917, **17**, 599; *J.*, 1918, 28A.

[99] U.S. Pats. 1255268 and 1255682; *J.*, 1918, 206A.

[100] *Analyst*, 1918, **43**, 161; *J.*, 1918, 299A.

[101] U.S. Pats. 1262938 and 1262939; *J.*, 1918, 334A.

[102] U.S. Pat. 1273110; *J.*, 1918, 581A.

[103] *J. Ind. Eng. Chem.*, 1918, **10**, 595; *J.*, 1918, 621A; and *J.*, 1909, 1036.

1450° C. only hydrated to the extent of 70% in six years, and it is probable that twenty years would be required for material prepared at the temperatures used in Portland cement manufacture.

BLEACHING POWDER.

The conditions relating to the production of bleaching powder are recorded by H. Ditz.[104] The conclusions arrived at by this author are recorded here at some length, as they appear to show far better the co-relation of laboratory results and works observation than the more scanty records of other writers.

The quality of bleaching powder in mechanically operated plants is determined by the concentration of chlorine in the gas and the presence of water. The most favourable condition is 10–12% chlorine for 36–37% bleach, the diluting air serving to moderate the reaction velocity and conduct away the heat of reaction. The gas must be dried by sulphuric acid, a wet gas causing a rise of temperature and consequent decomposition of the bleaching powder. The slaked lime should show 5–6% excess of water.[105] The function of the water appears to be to cool the reaction mixture by its own evaporation. On the supposition that the air leaving the plant at 40° C. is saturated with water, calculation shows that about 21% of the heat produced is carried off by this means, the remainder being lost by conduction and radiation. The 5–6% excess of water is not sufficient to saturate the air, but there is enough water set free by the first phase of the reaction

$$2Ca(OH)_2 + Cl_2 = CaO.\ Ca(Cl)OCl,\ H_2O + H_2O$$

to make up the deficiency. If the lime is dry at the start, water is obtained from the above basic compound, bringing about its decomposition with the liberation of chlorine The initial water in the slaked lime serves to prevent this. It appears possible that by using lime with 8–9% excess of water at the start, a better bleaching powder containing 39–40% available chlorine might be produced, but with so much water the lime is liable to form lumps into which the chlorine cannot permeate. The conditions prevailing in the chamber plant are different since the lime is not in motion. In mechanical plant it is likely that carbonic acid is more deleterious than when chambers are used. The decomposition of bleaching powder by carbonic acid is favoured by high temperatures and the presence of water and these conditions obtain in the higher drums of mechanical plant.

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[104] *Z. anorg. Chem.*, 1918, **102**, 66; *J.*, 1918, 148A.

[105] Schütz, *J.*, 1917, 546.

The chlorination of lime in an inclined cylinder (80′ × 20″) against a counter current of chlorine is the subject of a patent of The Castner-Kellner Co. and J. W. Moore.[106] A magnesium hypochlorite is prepared according to E. Merck[107] by treating magnesium oxide or hydroxide with hypochlorous acid or by chlorination of a solution containing excess of magnesia.

MANGANESE.

The discovery of a number of manganese ore outcrops has been reported, many of them apparently of high grade. Those occurring at Dagwin[108] on the Gold Coast, at Piracana in N. Brazil,[109] at Minas Geraes,[110] and at Cowichan Valley[111] in Vancouver Island appear to be noteworthy.

TITANIUM, ZIRCONIUM, TUNGSTEN.

Norske Aktieselskab for Elektrokemisk Industri[112] prepares titanic acid practically free from iron by boiling a solution containing quadrivalent titanium (and other metals, including iron) with a trivalent titanium compound, which may be either added as such or produced by reduction within the original solution. Thus a solution of titanium and iron, obtained by treating ilmenite with sulphuric acid, is electrolysed with a diaphragm and lead cathode until all the ferric iron is reduced to ferrous and about 5% of the titanic salts to the titanous condition. The current is then interrupted and the solution boiled, producing a white precipitate of metatitanic acid, the whole of the reduced titanium remaining in solution. A. J. Rossi and the Titanium Alloy Manufacturing Co[113] add a vegetable extract and a sufficient quantity of a calcium compound to nearly neutralise the free acid in a solution of titanium sulphate. The mixture is boiled and the precipitate separated.

The preparation of substantially pure zirconia and other compounds of zirconium has been patented by The Imperial Trust, R. T. Glazebrook, and others.[114] A mixture of crude zircon, fluorspar, and sulphuric acid is heated till fumes are evolved, the mass is agitated with water, decanted from the calcium sulphate, hydrochloric acid is added and then ammonia until the deposit of white basic zirconium sulphate forms. The precipitation continues without further addition.

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[106] Eng. Pat. 113457; *J.*, 1918, 206A.
[107] Ger. Pat. 305419; *J.*, 1918, 467A.
[108] *J.*, 1918, 57 R., 159R.
[109] *J.*, 1918, 154R.
[110] *J.*, 1918, 263R.
[111] *J.*, 1918, 394R.
[112] Eng. Pat. 108850; *J.*, 1918, 301A.
[113] U.S. Pat. 1272855; *J.*, 1918, 581A.

L. Bradford,[115] dealing with the properties of fused zirconia, states that its low coefficient of expansion and high thermal endurance, combined with resistance to crushing stress and hardness, place zirconia in the foremost rank as a refractory. Actual tests made at Remscheid on a Siemens-Martin furnace showed that after four months' working the hearth was in good condition and would serve for at least another four months. A saving of about 50% in actual maintenance costs as compared with firebrick lining was achieved. This goes far to offset the higher initial cost. E. H. Rodd[116] also gives a full account of zirconia.

The occurrence of wolframite ores[117] in the Kwantung Province of China is noted. The ore runs as high as 18% in veins of 10–18 inches in thickness. The production of tungsten in Portugal[118] shows a steady increase, amounting to 1457 tons in 1917. The average grade of the ore is given as 65%. A comprehensive survey of the tungsten resources of the British Empire is given in two highly interesting papers by S. J. Johnstone.[119]

ALUMINIUM.

The treatment of bauxites with a high silica content is described by W. B. Llewellyn and H. Spence.[120] The procedure is to some extent an amplification of previous methods.[121] The bauxite is crushed to pass ½ or ¾ inch mesh, and solutions of sulphuric acid or aluminium sulphate (with higher $SO_3 : Al_2O_3$ ratio than is desired) from previous operations are caused to circulate through it. The bauxite is preferably treated with solutions containing progressively increasing amounts of free acid and finally with weak liquors and water. If the silica content is high, previous ignition at a low red heat is advisable. More complete extraction is obtained, cost of powdering and filterpressing is avoided, and bauxites with high silica content can be economically dealt with and are in fact preferable. A lengthy description of the methods of preparation of alumina free from iron, silica, titanium, &c., for aluminium production is given by W. von Escher.[122] Amongst others the interesting Beyer[123] process is described, also the dry process, in which a high iron content is less injurious. The Peniakoff, Griesheim, and Serpek processes are also noted. In general, for material rich in iron but low in silica, the "dry" process (treatment with soda) is usual; in the reverse case the Beyer process. The latter is the most extensively used and appears to require less power and labour than others.

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[114] Eng. Pat. 112973; *J.*, 1918, 181A.
[115] *Chem. Trade J.*, 1918, **62**, 284.
[116] *J.*, 1918, 213R.
[117] *U.S. Cons. Rep.*; *J.*, 1918, 13R, 154R.
[118] *J.*, 1918, 152R.
[119] *J.*, 1918, 294R, 334R.
[120] Eng. Pat. 112881; *J.*, 1918, 149A.
[121] Eng. Pats. 3805 and 22950, 1912; *J.*, 1913, 366, 1066.

PERCHLORATES, PEROXIDES, HYDROSULPHITES.

The Aktiebolaget Carlit[124] suggest that in the manufacture of ammonium perchlorate from ammonium sulphate and sodium perchlorate the liquid be evaporated under reduced pressure at 45°–100° C., preferably beginning at 60° C. and rising to 80–85° C. The sodium sulphate is deposited in the anhydrous state without admixture of ammonium perchlorate.

The electrolytic methods used for the production of hydrogen peroxide are given in an article by E. B. R. Prideaux.[125] E. Merck[126] increases the stability of hydrogen peroxide solutions by distilling dilute commercial solutions with neutral organic or inorganic substances (*e.g.*, urea) without the necessity of concentrating or purifying the peroxide solution. A cyclic method of preparation from barium peroxide is given by F. Cobellis.[127] The barium peroxide is treated with phosphoric acid, and the resulting phosphate by treatment with nitric acid produces barium nitrate, which again in turn is utilised to prepare nitric acid and barium peroxide.

The Chem. Fabr. von Heyden[128] use reduced iron containing little carbon for the preparation of hydrosulphites or sulphoxylates from sulphurous acid. The resulting solutions are purer than when iron and carbon are used for the reduction. A. K. Gyzander[129] converts sulphites into hydrosulphites by the action of hydrogen under pressure.

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[122] *Chem.-Zeit.*, 1918, **42**, 353, 361; *J.*, 1918, 504A.
[123] *J.*, 1888, 625, 748; 1893, 263, 353, 925.
[124] Eng. Pat. 110544; *J.*, 1918, 301A.
[125] *J.*, 1918, 257R.
[126] Ger. Pat. 303680; *J.*, 1918, 371A.
[127] U.S. Pat. 1273824; *J.*, 1918, 622A.
[128] Ger. Pat. 304107; *J.*, 1918, 371A.
[129] U.S. Pat. 1270150; *J.*, 1918, 545A.

RARE EARTHS, ARGON, RADIUM.

A variety of salts have been suggested as offering advantages in the fractional crystallisation of rare earths. L. Jordan and B. S. Hopkins[130] describe the method of separating gadolinium, europium, and samarium by the successive use of the bromates, dimethylphosphates, and glycollates. The concentration of dysprosium and holmium, using ethylsulphates and bromates, was achieved by H. C. Kremers and C. W. Balke[131] after more than 150 recrystallisations. L. F. Yntema and B. S. Hopkins[132] studied the fractional hydrolysis of the phthalates of yttrium-holmium material, but found the nitrite method preferable both as regards cost and efficiency. A general survey of the occurrence and utilisation of the components of monazite is given by S. J. Johnstone.[133]

The Welsbach Co.[134] recover thorium from monazite sand as pyrophosphate by treating with concentrated sulphuric acid and heating sufficiently strongly to convert the ortho- into the pyro-phosphate. On treatment with water, the pyrophosphates of the rare earths remain in solution and the insoluble thorium pyrophosphate is obtained fairly pure by decantation.

G. Claude[135] describes the industrial preparation of argon by the re-liquefaction of the oxygen-argon-nitrogen fraction of liquid air. The gases, cooled by liquid oxygen, are freed from nitrogen and the resultant liquid mixture of oxygen and argon re-distilled in a column, so that oxygen is condensed and argon passes on, producing a gaseous mixture containing 75–80% argon, 1–2% nitrogen, and the remainder oxygen which can be removed by means of hydrogen.

R. Cable and H. Schlundt[136] give the course of treatment adopted in working up the pitchblende ores of Gilpin County, Colorado. The ore, uraninite associated with pyrites, after preliminary concentration and grading, is heated in chlorine to produce sulphur chloride and a chloride sublimate which contains nearly all the radium. The discovery of proto-actinium, the parent of actinium, has been reported.[137] It may be isolated from pitchblende residues insoluble in acids after the removal of all but the tantalum group. The yield from 1 kilo of residue was 73 mgrms. as a white powder.

[130] *J. Amer. Chem. Soc.*, 1917, **39**, 2614; *J.*, 1918, 55A.

[131] *J. Amer. Chem. Soc.*, 1918, **40**, 593; *J.*, 1918, 300A.

[132] *J.*, 1918, 654A. [133] *J.*, 1918, 373R.

[134] Eng. Pat. 112380; *J.*, 1918, 83A.

[135] *Comptes rend.*, 1918, **166**, 492; *J.*, 1918, 241A.

[136] *Met. and Chem. Eng.*, 1918, **18**, 460; *J.*, 1918, 333A.

[137] *Münchener Neuste Nachrichten*; *J.*, 1918, 263R.

ACETIC, FORMIC, AND OXALIC ACIDS.

H. Dreyfus[138] has taken out two patents relating to the production of acetic acid from acetaldehyde. Improved yields are claimed for catalysis in reaction chambers maintained at temperatures above the boiling point of acetic acid, preferably 150°–200° C. Suitable catalysts are platinum, copper and copper compounds, chromium compounds, and many others. Although catalysts facilitate the reaction they are not essential for complete oxidation. The Akt. Ges. für Anilinfabr.[139] suggest the dehydration of dilute acetic acid by monohydrated magnesium sulphate (Kieserite) in the presence of a solvent such as chloroform, di- or tri-chloroethane, or benzene. A. Lackman[140] prepares sodium formate by passing granular caustic soda through a heated tubular conduit in a direction contrary to that of a pre-heated gas containing carbon monoxide. Sodium oxalate may be prepared in a similar manner at a higher temperature. The waste gases are used for heating. C. T. Thorssell and H. L. R. Lunden[141] describe a process for the separation of sodium oxalate from a mixture of sodium oxalate, carbonate, and hydroxide by treatment with a solution containing sodium bisulphate and sulphuric acid. The acid oxalate is partially separated by crystallisation and the remainder by conversion into an insoluble oxalate.

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[138] Eng. Pats. 105065 and 108459; *J.*, 1918, 180A, 266A.

[139] Ger. Pat. 302673; *J.*, 1918, 370A.

[140] U.S. Pat. 1274169; *J.*, 1918, 622A.

[141] U.S. Pat. 1251938; *J.*, 1918, 123A.

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GLASS; REFRACTORIES.

By W. J. Rees,
Department of Refractory Materials, University of Sheffield.

Glass.

The importance of the glass industry to the national welfare has been rendered very apparent during the progress of the war. For essential items of the equipment of our naval, military, and medical services, glass is a direct necessity. The call for many of these has had to be met by the cultivation of new branches of glass manufacture, and the success which has been realised under very difficult conditions is one of the noteworthy industrial achievements of the war. It is greatly to be desired that these new branches of manufacture should be retained and supplemented, so that the country may remain independent of foreign supplies. The interest in the scientific aspects of glass-manufacture is growing, and the application of scientific methods is rapidly gaining ground and tending to place the reviving industry on a surer foundation. Discussions in the German press have indicated the real importance attached to the glass industry as a national asset; and in a recent article in the *Frankfürter Zeitung* it is contended by A. Feiler that, in facing the necessity for a rapid resuscitation of exports from Germany, its glass industry should come second only to the chemical industry. Many problems are involved in the economic production of glass, but the essentials lie in the composition and physical and chemical properties of the glass itself, and in the inherent properties of the refractory materials available for building the containing-vessels and the furnaces for glass-melting. Much useful research work is in progress in the Department of Glass Technology of the University of Sheffield, at the National Physical Laboratory, and in the laboratories of the larger works; and the rapid growth of the Society of Glass Technology is a good augury for the future.

The use of automatic and semi-automatic glass-making machinery for all kinds of small glassware is developing rapidly, with a resultant large increase in output and an important reduction in the cost of production. The patent registers of both this and other countries indicate the increasing attention which is being given to the general mechanical appliances of the glass industry. H. H. Pitt,[1] in a review of American methods and practice, describes types of automatic and semi-automatic machinery in present use, and indicates improvements which have been made, leading to greater uniformity of production. It is suggested that much of the American success in the manufacture of high-quality pressed ware is due to the excellent condition in which the presses and moulds are kept. Reference is also made to the use of clay-nosed gathering-irons for facilitating the quick and accurate gathering of small quantities of glass. The adoption of automatic machinery with blowing-devices has revolutionised the manufacture of bottles, and is likely to have an equally important effect on the production of such articles as jars, tumblers, lamp-chimneys, electric-lamp bulbs, &c. The machine-production of sheet-glass is making rapid headway in America. Two methods are in use: in one, of which the Colburn process is an example, flat sheets of glass are drawn directly from the metal in the tanks and pass continuously into and through the lehr, being cut to size on passing out at the cold end; in the other, of which the Frink process is an example, the glass is drawn from the tanks in the form of large cylinders, which are cut into lengths and subsequently split and flattened by the ordinary methods. The average quality of the sheet-glass produced is not yet equal to that of English sheet-glass made by the older methods; but the improvements, since the original introduction of mechanical methods, are such that the eventual general adoption of mechanical production is likely. The success which has been achieved in America by the use of mechanical methods for general glass-production will undoubtedly stimulate manufacturers in this country to forge ahead in this direction.

During the year under review, progress has been made in the substitution of gas-fired furnaces for the older, uneconomical, coal-fired furnaces. Recuperative furnaces are finding favour, because of the lower labour costs in attending them; and in several types, temperatures of 1400°–1450° C., sufficient for the founding of complex-resistant and other glasses, can be efficiently maintained. With increasing efficiency of recuperation, the development in the use of this system—especially for pot-furnaces—will be rapid. R. L. Frink,[2] in discussing the operation of tank-furnaces, refers to the importance of the proper

[1] *J. Soc. Glass Tech.*, 1918, 2, 19.

[2] *Trans. Amer. Ceram. Soc.*, 1917, 19, 331; *J.*, 1918, 507A.

regulation of the dampers, and to the advantages of ports in which the gas and air are thoroughly mixed before combustion. In regenerative-furnaces, it is pointed out, the temperature of the upper parts of the regenerators should not be less than 1200° C. There is no doubt that by the proper balancing of a furnace, and the maintenance of high regenerator-temperatures, a considerably increased efficiency is secured.

Annealing.—Much attention has, during the year, been of necessity given to the question of adequate annealing, as some of the British glassware was inferior to the imported ware which it has replaced. Very definite improvements can be recorded; and these are in large measure due to the work on the methods of determining annealing-temperatures, carried out by Twyman and in the Department of Glass Technology of the University of Sheffield. It is desirable that an effort should be made to define the permissible amount of stress which may remain in glassware for given purposes without detrimental effect. S. English and W. E. S. Turner[3] have pointed out that, in order to avoid the occurrence of strain in glassware, it is essential to determine: (*a*) the temperature at which strain can be removed rapidly, without causing deformation of the glass; (*b*) the lowest temperature at which for practical purposes the strain can be removed; (*c*) the maximum rate of cooling between these two temperatures which will not cause a recurrence of strain. Determinations were made of the rate at which annealing occurs at different temperatures. In a glass with an upper annealing temperature of 630° C., it was found that, at 600° C., strain was completely removed in 4½ hours; and that between 600° and 630° C., each rise of 5° C. approximately halves the time required for annealing. From the experimental results it is obvious that there may be great variations in the rate of annealing for comparatively small alterations in temperature. The practical importance of these results is great, as indicating the effect of fluctuations in lehr temperature on the annealing of glassware. A simple mechanical method for determining the annealing temperature of glass is described. It is based on the fact that there is a relation between the disappearance of strain in a viscous substance and the deformation of the same substance under constant stress. A rod of the glass is secured at one end and slightly weighted at the other, and the temperature at which the rod undergoes fairly rapid bending is observed. The rate of bending and the rate of annealing are plotted for a number of glasses, and it is shown that they run parallel to each other. F. Twyman[4] has described a small apparatus based on the same principle: it is placed in the annealing-chamber, together with the articles to be annealed, and when the weighted end of the glass rod has sunk a certain distance, it is known that the annealing has reached a certain pre-determined stage or is completed. English and Turner further discuss the rate at which annealed glass can be cooled with safety. Lehrs are often so arranged that the fall in temperature along them is uniform; but it is evident that just below the annealing-temperature the glass may be cooled comparatively rapidly, and that, as it stiffens, the rate of cooling must be decreased and remain slow until the glass is rigid. For instance, it was found possible to cool a glass with an upper-annealing temperature of 585°–590° C. at the rate of 25° per hour between 590° and 500°, but at only 9° per hour between 500° and 400° C. Below 400° C. the rate of cooling could be much increased. Methods are described for determining the temperature at which the rapid cooling of a glass may commence. In order to pass glassware through the lehr as quickly as possible, it is necessary to vary the rate of passage at these different stages. Chemical composition has a marked effect on the annealing-temperatures of glasses, and it is therefore undesirable to pass glasses differing in composition to any great extent through the lehr together. The most difficult glasses to anneal satisfactorily are the complex ones—such as are used for chemical ware. Borax acts as a flux in molten glass, and also tends to reduce the coefficient of expansion of glasses containing it; and although these factors should apparently facilitate easy annealing, they are of less importance than the rate at which the viscosity of the glass varies throughout the annealing range.

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[3] *J. Soc. Glass Tech.*, 1918, **2**, 90.

[4] Eng. Pat. 114183; *J.*, 1918, 242A.

M. So[5] has made some interesting observations on annealing-phenomena. A newly drawn glass-fibre was heated slowly in an electric furnace, and its length observed. This increased as the temperature rose; but in the region of 400° C. it began to diminish, and at about 500° C. the glass became plastic. The precise effect varied with the nature of the glass, but was not exhibited by annealed specimens. It was further observed that when either annealed or unannealed glass is slowly heated or cooled, the curve of temperature-change shows that over the plastic range of temperature there are absorption and liberation of heat, indicating that some change of state of a constituent of the glass takes place at that temperature.

G. V. Wilson,[6] in a valuable and suggestive paper, has put forward the results of an investigation of crystalline products formed by direct crystallisation from masses of molten glass and resulting from

[5] *Proc. Tokyo Mathematico-Physical Soc.*, Sept. 1918.

[6] *J. Soc. Glass Tech.*, 1918, 2, 177; *J.*, 1918, 691A.

the interaction of the molten glass with the refractory materials containing it. The paper is one which will repay careful study by those concerned with the actual manufacture of glass, as many of the facts elucidated have a very distinct bearing on the composition of glass-batches and on the formation of protective coatings which will retard the corrosion of pots or tank walls. In the examination of specimens of crystalline material obtained from such sources as: (*a*) a mass of molten glass which had, through solvent action, burst through the floor of a tank-furnace and slowly cooled in a confined space below; (*b*) the corroded faces of tank-blocks; and (*c*) the inner and outer surfaces of used glass-house pots, certain common rock-forming minerals, the presence of which was revealed by petrological investigation, have been identified. From their origin, these minerals are classified into three main groups: (1) those formed by direct crystallisation from molten glass—namely, wollastonite, tridymite, quartz, and augite; (2) those formed by the action of the molten glass on fragments of undecomposed limestone—namely, wollastonite, augite, melilite, &c.; and (3) those formed by the action of glass, or the glass-batch materials, on the clay of which the pots and furnaces are constructed—namely, sillimanite, corundum, magnetite, biotite, and felspar. It is shown that, under certain conditions, the minerals of Group 1 may all crystallise from the same melt. The formation of the minerals of Group 2 is compared with the contact alteration of limestones by igneous rocks. In discussing the mode of formation of the minerals of Group 3, it is shown that the separation of particular minerals is determined by the relative proportions of SiO_2, Al_2O_3, and Na_2O present; and that the conditions governing the formation of sillimanite and corundum are well defined. In glass-house pots, which had lasted well, a considerable development of sillimanite was almost invariably found, and the value of the use of highly aluminous clays is suggested. Examination of used pots indicated that in those made from aluminous clays, the surface network of sillimanite formed acted as a protective coating, and prevented rapid corrosion of the pot; with siliceous clays, sillimanite does not crystallise or is absorbed practically at once, and the rate of corrosion is considerably increased. The life of a pot appears to depend on the balance between the rate of formation and of solution of the sillimanite layer—that is to say, it is dependent on the degree of saturation, with respect to alumina, of the molten layer in immediate contact with the pot body. A point of great practical importance referred to is the desirability of finely crushing any solidified glass for remelting—such as that from tanks which have been let out for repair—which contains any considerable quantity of wollastonite. The reabsorption of wollastonite (inverting at 1200° C. into pseudo-wollastonite) into a glass-melt takes place more by slow solution than by direct fluxing action, and is therefore facilitated by presenting as large a surface as possible to the action of the solvent. A particularly interesting occurrence of tridymite from the chilling and subsequent effort to remelt the second filling, during the founding of a 50% lead glass, is noted.

In a continuation of work on the effects of the addition of alumina to a glass-batch, it is shown by F. Singer[7] that its addition renders the melt more fusible, the effect being marked with the addition of only 0·05 mol. Al_2O_3. It is suggested that the limits for the beneficial use of alumina vary for particular types of glass, and are low with heavy lead-glasses. The joint effect of alumina in increasing fusibility and in reducing the tendency to devitrification renders it a particularly valuable ingredient of a glass-batch. The addition of fluorspar to a glass-batch[8] also increases its fusibility and, in addition, assists in fining the glass, as silicon fluoride is formed and evolved at a high temperature. Its corrosive action on the pots is, however, a detriment, and renders its use undesirable except, in conjunction with felspar and china-clay, as an opacifier. W. Frommel[9] claims that glasses decolorised by selenium are more brilliant than similar glasses in which manganese or nickel oxides have been used as decoloriser. Since its decolorising action is due to the presence of the element in colloidal solution, it can only be used with advantage under reducing conditions, as it is oxidised readily. Glasses decolorised by selenium assume a brown tinge on prolonged exposure to bright sunlight.

The best method of removing small bubbles or "seeds" from molten glass is by introducing larger ones (*e.g.* by immersing a potato in the glass); the small bubbles merge into the large ones, and are so carried to the surface. R. M. Howe[10] discusses the principles controlling the removal of bubbles, and concludes that it depends on the frictional resistance of the glass and the size of the bubbles. An equation $x = Ar^2/K$ is deduced, where x is the rate of removal, r the radius of the bubbles, A a constant, and K the frictional constant. As K can never be made negligibly small it is impossible to remove all the small bubbles by raising the temperature of the glass. With some types of glass it is undesirable to use these "boiling-up" methods of eliminating bubbles as the foreign matter introduced may affect the colour of the glass; but by careful attention to the mixing of the batch and to the founding process, the tendency to the formation of fine "seeds" may be controlled.

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[7] *Ker. Rundschau*, 1917, **25**, 142.

[8] *Ker. Rundschau*, 1917, **25**, 63; *J.*, 1918, 508A.

[9] *Ker. Rundschau*, 1917, **25**, 95; *J.*, 1918, 583A.

[10] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 201; *J.*, 1918, 508A.

Scientific and Illuminating Glassware.—A comparison of the exhibits at the exhibition held by the Chemical Society in November 1915, with those at the British Science Guild's exhibition in August 1918, showed to a marked degree the very considerable progress which has been made in the home production of special glassware. In scientific glassware an all-round improvement in durability can be noted, due both to an increased regularity in thickness and to much closer attention to the annealing processes. Attention is also being given to the production of lamp-blown and graduated ware, and the supply of these very necessary articles is increasing in both quantity and quality. Difficulties have been many, but the majority of the problems involved have been successfully solved. Exhaustive tests have proved that the British-made glassware is quite equal in general qualities to the imported ware, whilst in its resistant properties it is distinctly superior. The National Physical Laboratory is inaugurating a special department for the testing of volumetric glassware and the general standardisation of scientific glassware, and there is every indication that these facilities will be largely utilised by those manufacturers who are laying themselves out to produce an adequate supply of reliable graduated apparatus. Committees of the Department of Scientific and Industrial Research and of the Society of Chemical Industry have under consideration the question of the standardisation of sizes of chemical glassware. A reduction in the number of sizes and shapes of beakers, flasks, &c., might well be made without inconvenience to the users, and the resultant simplification would be a benefit to both the consumer and manufacturer. The standardisation of illuminating glassware, both in respect to size and essential properties for particular purposes, is also under consideration by the Society of Illuminating Engineers and the Society of Glass Technology. The Technical Physics section of the Reichsanstalt[11] suggest that resistant glassware for illuminating purposes should be classified on the basis of its mean coefficient of linear expansion between 0° and 100° C. It is suggested that only those glasses with a coefficient of linear expansion less than 35×10^{-7} should be placed in the first grade. The production of this type of high-grade glassware is making rapid strides in this country, and there is little doubt that, as labour becomes available, the supplies will be such as to render importation unnecessary. In these branches of the glass industry there is also very considerable activity in France, America, and Japan; so that the market for the German and Austrian ware is likely to be a much more restricted one than in pre-war days.

[11] *Sprechsaal*, 1917, **50**, 90.

F. D. Cauwood and W. E. S. Turner[12] have continued their investigation of the resistant properties of numerous examples of English and foreign chemical glassware, and both their results, and the results of similar investigations made by P. H. Walker and F. W. Smither,[13] indicate that the best glasses for general work are those of the zinc-aluminium-borosilicate type. For special purposes and for chemical research it may be desirable to use various glasses whose composition confers resistance to the attack of particular reagents: for instance, certain of the lime-soda glasses, whilst not very resistant to water or dilute alkalis, are in their resistance to acids the best glasses available.

The need for a glass suitable for goggles for the examination of highly incandescent bodies is now satisfied to a considerable extent by the production of a glass known as "arc-screen." The results of further research work on the production of glasses opaque to ultra-violet radiation are embodied in a patent specification.[14] Titanium oxide and vanadium oxide are effective in reducing the transmission of the ultra-violet radiation, and their use either alone or in conjunction with cerium oxide (as used by Sir William Crookes) is suggested. It is to be noted that with vanadium oxide, reduction of the higher oxides to the lower, reduces the opacity to the ultra-violet radiation. It had been previously pointed out by Sir William Crookes[15] that iron in the higher state of oxidation confers on a glass opacity to ultra-violet radiation; whilst a glass containing it in the lower state of oxidation transmits the ultra-violet, but is opaque to infra-red radiation. It will be of considerable interest to note if further investigation presents other analogies of this type.

Optical Glass.—The manufacture of optical glass was commenced in this country so long ago as 1848, and it proved of immense importance that its production here was still alive at the outbreak of war, although the supplies were limited. It is very greatly to the credit of the firm of glass manufacturers responsible for almost the whole of the production, that the home demands, and also, to a considerable extent, those of our Allies, for all the types of optical glass necessary for war munitions have been successfully met. The successful experimental work conducted in the laboratories of this firm, on which the whole of the production of new types of glass has been based, is noteworthy among the many technical achievements during the war. The list of glasses available has been so extended that in this, as in other branches of glass manufacture referred to, the consumers may be quite independent of foreign supplies. Small, but increasing, quantities of the principal types of optical glass have also been available from another firm, whose technical staff have successfully solved some of the many problems involved in the production of homogeneous glass with optical properties uniform in successive meltings.

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[12] *J. Soc. Glass Tech.*, 1918, 2, 219, 235; *J.*, 1918, 692A.

[13] *J. Ind. Eng. Chem.*, 1917, 9, 1090; *J.*, 1918, 89A.

[14] Corning Glass Works, Eng. Pats. 118397 and 118398; *J.*, 1918, 584A.

[15] *Phil. Trans.*, 191, 211.

The production of new types of glass of complex composition has emphasised the need for a simple system of nomenclature for optical glasses. It has been recently suggested by W. Zschokke[16] that these glasses should be divided into four groups: "Crown," "Flint," "Barion," and "Barint" (the two last being contractions of "Barium-Crown" and "Barium-Flint"); the individual glasses in each group becoming characterised by affixing two numbers, indicating the optical properties—*e.g.* a crown glass of refractive index 1·507 and dispersive power (the ν of Abbe) 62·8, is indicated by "Crown 507/628."

REFRACTORIES.

The Society of Glass Technology has appointed a Refractories Research and Specifications Committee to direct a comprehensive scheme for research on the refractory materials used in the glass industry. It is intended on the completion of the laboratory investigations to make final tests on such a scale that the essential conditions of commercial glass-production shall be satisfied, and then to issue a series of standard specifications for the various refractory materials used in the glass industry. The refractories for furnace construction and for the glass-containers are one of the heaviest charges in the manufacture of glass, and the extent to which the efficiency and life of a furnace are dependent on the character and behaviour of the refractory materials used is not generally recognised. There is at the present time a very serious lack of definite information to guide manufacturers in their choice of refractories, and although, in the majority of works, practice is based on costly experience, variations in practice are considerable. The introduction of higher-temperature furnaces for the manufacture of types of glassware for which this country has been hitherto dependent on foreign sources of supply, has emphasised our lack of definite information on these vital points. Thorough systematic investigation is a prime necessity, and the vigorous action of the Society of Glass Technology is therefore very timely. It is of interest to note that this research scheme has the active support of the Optical Munitions and Glassware Supply Branch of the Ministry of Munitions. Experience during the war has shown this department the dependence of efficient production and continuity of working on the refractories used for furnace-construction and pot-making.

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[16] *Z. f. Instrumentenkunde*, 1918, 38, 49; *J.*, 1918, 417A.

The adoption of standardised methods of testing is an essential preliminary to the production of any specification. The conditions should be such that from the behaviour of the samples under the tests, predictions may be made as to the behaviour of the particular material in service. The ideal test will naturally be one made in the works under the normal conditions of use and with adequate records of all furnace conditions. Unfortunately, however, tests of this type take much too long a time for them to be of use in formulating an opinion as to the quality of any particular consignment. In addition, diverse reports from works' trials are not an unusual experience, as small differences in the details of furnace-construction may cause very decided differences in furnace conditions. Varying results of tests made in different laboratories are also not uncommon; so that emphasis is laid on the importance of standardising the methods of test. The general adoption of the standard tests, suggested by the Refractories Section of the Ceramic Society,[17] will do much to co-ordinate and speed up the researches which are now in progress at the various centres referred to in the previous report. The analytical methods recommended are well-known ones for the accurate complete analysis of the various materials, and will be generally accepted. It would be an advantage, however, if consideration could be given to many of the shortened methods of analysis in use in works and other laboratories, as the standardisation of these methods also would be of general utility. The physical tests prescribed are, to some extent, based on those carried out, under the guidance of Dr. J. W. Mellor, by the Refractory Materials Committee of the Institution of Gas Engineers in preparing the standard specifications for refractory materials used by the gas industry. The apparatus necessary for carrying out these physical tests is necessarily of an elaborate nature, and to ensure comparable results it may be found desirable in some measure to standardise the apparatus as well as the routine of the tests. As pointed out by C. Johns,[18] the determination of volume-changes, normal refractoriness, and crushing-strength at high temperatures, involves the question of temperature-determination and of the rate of heating employed in the test. The use of Seger cones is recommended, because, like the materials under test, they have no distinct fusion-point, but an extended softening range ; and the rate of heating is defined. J. W. Mellor has shown[19] that if the temperature of refractory materials is rapidly increased, they appear to soften

[17] *Trans. Ceram. Soc.*, 1918, 17, 300 ; *J.*, 1918, 693A.

[18] Iron and Steel Institute, Autumn Meeting, 1918.

[19] *Trans. Ceram. Soc.*, 1918, 17, 91 ; see *J.*, 1917, 1128.

at a higher temperature than if slowly heated, because equilibrium is not reached throughout the mass at any temperature before it is raised to a still higher temperature. The faster the rise of temperature, the more pronounced is this effect. The normal refractoriness, therefore, of a material for one rate of rise of temperature, for instance, will not correspond with that determined for another rate of rise of temperature. The importance of explicitly defining the rate of heating is obvious. The question as to whether it is more desirable to measure actual temperatures of tests by a pyrometert han to depend on the behaviour of Seger cones has been frequently discussed. At present the weight of opinion is in favour of the use of Seger cones as indicators, because the observed effects occur over a range of temperature and not at any specific temperature. A clearer meaning will be attached to the statement that " the softening point is equivalent to that of cone 32 " than to " the softening point is 1710° C." Almost the most important test standardised is that of refractoriness under load, and it may well be desirable that in this test the actual temperature should be measured by a pyrometer and the deformation referred to a measured stress at a definite temperature. For instance, the definite temperatures at which a material fails under a load of (*a*) 25 lb. per square inch, (*b*) 50 lb. per square inch might be taken as the basis of expressing the effect of load on refractoriness.

J. W. Mellor and W. Emery,[20] in determining the effect of load on the refractoriness of a number of firebricks, used the standardised method for making this test. Tests of twenty fireclay bricks, with a normal refractoriness equivalent to Seger cones 26 to 33, were made under a load of 50 lb. per square inch at the temperatures at which cones 14 to 26 squatted. Most of the samples showed a steady deformation throughout the heating. Similar tests on six silica bricks, the normal refractoriness of which varied from cones 29 to 34, were made under the same load at cones 3 to 31. Four of the samples collapsed suddenly, and the other two more steadily; the coarser grained bricks behaving more steadily. A critical examination of the results of these tests under load is necessary, as the worst result (collapse at cone 3 under the load) was obtained with a soft, red, silica brick of fine, even texture, which had given satisfactory service in gas-retort settings. It is considered that a load of 50 lb. per square inch is too severe for fireclay bricks, and one of 20 lb. to 30 lb. per square inch is suggested. The collapse under load is apparently of two orders: fusion collapse, due to the gradual softening of the matrix, and mechanical collapse of an abrupt nature. The former predominates in fireclay, bauxite, and zirconia bricks, and the latter in silica, magnesite, and chromite bricks. A fireclay brick with silica grog gives a higher test under load than one without grog. Some of the least resistant bricks became much more resistant when re-fired at cone 15 to 16 for two hours, collapsing at cone 14 instead of cone 9. Probably by burning at a higher temperature the fluxed matrix dissolves more of the less fusible constituents of the brick and thus increases in viscosity. This provides a strong argument for higher kiln-temperatures in the burning of refractories.[21] It has been suggested that a better classification of the resistance of firebricks to load may be made by applying the pressure by means of a spring, so that the load diminishes when the brick begins to yield.[22] A test under diminishing pressure in some respects supplies a closer resemblance to service conditions than a test under constant load.

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[20] *Gas J.*, 1918, **142**, 478; *J.*, 1918, 371A; *Trans. Ceram. Soc.*, 1918, **17**, 360.

It is an extremely difficult matter to devise a standard test for the corrosive action of flue-dusts on refractory bricks which will enable quantitative results to be obtained. Corrosion and slagging from the action of dust from such sources as coal-ash, furnace-charges, &c., is a common cause of the rapid deterioration of bricks. It is frequently very much in evidence in regenerator-bricks, and may be a source of much trouble in the recuperator-flues of recuperative-furnaces. When the dust is of such a composition that it forms a glaze on the bricks, a protective coating may be formed and the rate of attack very considerably diminished. If, however, the glaze formed is fluid at the temperature employed, and is able to flow away, corrosion will take place rapidly. Attempts have been made to form a resistant face on bricks by the use of special refractory glazes, by actual fusion of the surface[23] of specially compounded bricks, and by applying a mixture of carborundum with about 10 % of fireclay (or silicate of soda) in the form of a paint. This latter method has proved of considerable value in increasing resistance to the abrasive action of dusts and hot gases. A method devised by Mellor and Emery[24] is suggested as the basis of a standard method of test. In this method the action of the dust is accelerated and exaggerated, so that effects which might take months to become evident in an industrial furnace, are obtained in a few hours. The difference in the conditions of test and the conditions of use will be, however, so marked, that in some cases the accelerated results may lead to inaccurate conclusions. The furnace used is heated by a Brayshaw burner using town gas, with an air-blast of 3 lb. to 4 lb. pressure, and is so arranged that the bricks can be exposed to the action of dust under controlled conditions. The dust, ground to pass a 60's lawn, is injected through the burner, and the dust-charged flame impinges directly on the brick to be tested. The dusts used in the experimental work were boiler-flue dusts, ochreous dust from a gas-retort bench, dust from the slag-chamber of a steel melting-furnace, dust from a blast-furnace Cowper stove, "bull-dog," red hæmatite ore, tap-cinder, lime, lime and common salt (1 : 1), salt, sodium sulphate, salt and felspar (1 : 1), and sodium silicate and calcium silicate (1 : 1). It was found that, in general, the dust penetrates more readily into fireclay than into silica bricks, and that in most cases the bond is attacked first and the coarser grains last. The depth of penetration was less in fine-grained silica bricks than in coarser-grained bricks. Under oxidising conditions, iron oxide does not corrode silica bricks to any extent, but under reducing conditions ferrous silicate is formed and causes rapid corrosion. The dusts apparently influence the conversion of the quartz in a silica brick into the forms of lower specific gravity, even when there has been no visible penetration of the coarser grains. These latter results are of considerable interest in their bearing on the influence of "impurities" in the silica brick itself on the behaviour of the brick under normal conditions of use. Another method which has been suggested for testing the effect of dust on refractories is to mould mixtures of the dust and the ground refractory, in definite proportions, in the form of cones, and then to determine the softening point.[25] A comparison of results obtained by the two methods might furnish data of considerable interest.

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[21] See also *Trans. Amer. Ceram. Soc.*, 1917, **19**, 248; *J.*, 1918, **508A**.

[22] J. B. Shaw, *Trans. Amer. Ceram. Soc.*, 1917, **19**, 498; *J.*, 1918, **510A**.

[23] See A. Reynolds, Eng. Pat. 111355; *J.*, 1918, **31A**.

[24] Ceram. Soc., Oct. 1918; *J.*, 1918, **693A**.

C. E. Nesbitt and M. L. Bell [26] concluded from the results of impact, abrasion, spalling, slagging, and compression tests that firebricks tended to group themselves according to their density. With bricks of the necessary refractoriness, those of high density had generally the best resistance to abrasion and slags. The effect of pressure and moisture in producing density was investigated. Tests were made with a standard fireclay mixture, and the mechanically held water was varied from 4% to 12%, the bricks being formed under a pressure of 2000 lb. per square inch and burned in the usual manner. The densest bricks were obtained with water-contents in the clay mixture of 6% and 8%, and these bricks had a greater resistance to slag penetration than the bricks made with clay of lower and higher water-contents. A comparison of the resistant properties of bricks made under high and low pressures was much in favour of the high-pressure brick.

A. Reynolds [27] has referred to experiments carried out at the River Don Works, Sheffield, on the occlusion of gases in firebricks. Crushed

[25] *Trans. Ceram. Soc.*, **1913, 13,** 12.

[26] *Met. and Chem. Eng.*, 1917, **17,** 184 *J.*, 1917, 1048.

[27] *Trans. Ceram. Soc.*, **1918, 17,** 385 *J.*, 1918, 701A.

bricks were heated in vacuum at a temperature of 900°–1000° C., and any gas evolved was extracted by a Sprengel pump. Small quantities of gases (mainly CO_2) were obtained. The apparatus is not described, so that possible experimental errors cannot be estimated; but the results are certainly suggestive in their bearing on some of the phenomena of overfiring and bloating. R. J. Montgomery and C. E. Fulton,[28] in investigating the relation between the softening point and composition of fireclays, plotted the ratio of alumina to alumina *plus* silica as abscissæ, and the softening points as ordinates. These points all lie below the eutectic curve, found by R. B. Sosman,[29] for mixtures of pure alumina and silica. The vertical separation between such points and the curve appears to depend primarily on the proportion of fluxes in the clays. The maximum activity of the fluxes was observed in a clay containing 14 % of alumina (alumina *plus* silica equalling 100). With high silica, beyond the eutectic point, the activity of the fluxes diminishes rapidly.

H. V. Thompson [30] records results obtained in a series of experiments made to determine the hydrolysis of salt in the neighbourhood of 1100° C. The salt was volatilised at 1100° C. in currents of dry and moist air, and under the conditions of the experiment 1 grm.-mol. of water-vapour decomposed 0·37 grm.-mol. of salt. Chips of quartz exposed to the action of the salt-vapours were superficially attacked with the formation of an insoluble silicate—the effect with moist air being much more pronounced than with dry air. A black crystalline form of magnetic oxide was formed as the result of heating ferric oxide in the current of salt-vapour. Alumina was superficially attacked with the formation of an aluminate. Tentative experiments made with clays indicated a more vigorous action than with the pure constituents, the effect increasing with increase of the iron-content of the clay. This work has an important bearing on the corrosion of coke-oven linings, much of which is directly due to the salt-contents of the coal. This corrosion may conceivably be due both to sodium oxide and to free chlorine. The direct formation of ferric chloride, by the action of chlorine, and its subsequent oxidation to ferric oxide, would give rise to some of the phenomena observed in the examination of corroded coke-oven linings. Very similar phenomena have been observed in electrical steel melting-furnaces having electrodes in the manufacture of which saline oil cokes were used.[31]

A refractory material of considerable utility in various directions is now available by the development of the bauxitic clays which overlie the Millstone Grit havas series in north-west Ayrshire.[32] The clay is very hard and well jointed, has a conchoidal fracture, and contains numerous small spherules of a highly aluminous material. It is almost non-plastic, so that a proportion of plastic refractory clay must be added to provide a bond. Samples from various locations contain up to 50% of alumina and up to 10% of titanic oxide, and have softening points of from cones 32 to 38. Bricks made from this material are giving good results in such positions as the ports of gas-fired furnaces, where high refractoriness, coupled with good resistance to abrasion, are desirable factors. W. J. Rees[33] directs attention to the successful use of bricks of this type in the crown of a small Greaves-Etchells electric furnace. Under certain conditions, which are under investigation at the present time, this clay is readily corroded.

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[28] *Trans. Amer. Ceram. Soc.*, 1917, **49**, 303; *J.*, 1918, 508A.

[29] *J.*, 1917, 136.

[30] *Trans. Ceram. Soc.*, 1918, **17**, 340; *J.*, 1918, 333A.

[31] H. Scragg, *J.*, 1918, 123T.

The very recent discovery of the utility of this deposit lends point to the suggestion of W. G. Fearnsides[34]—that between the rock-beds and the geological horizons which are already being worked to supply existing demands, there occur many other beds, the composition and refractory qualities of which are quite unknown. It is quite likely that a systematic chemical survey of the clays occurring throughout the Carboniferous System would reveal materials with properties such as would render them of value for some particular purpose.

Not the least useful part of the work which the Refractories Section of the Ceramic Society undertakes is that of obtaining from competent geologists, papers dealing adequately with the native supplies of refractory materials in, or contiguous to, the districts in which high-temperature furnaces are an essential part of the industrial equipment. The districts already dealt with include the Potteries, South Staffordshire, the South of Scotland, the Sheffield district, and South Wales.

Glass-house Pots.—The problems relating to glass-pots fall naturally into two categories: those having to do with the building of the pots and their treatment up to the time of transferring to the pot-arch, and those concerning the subsequent treatment and behaviour. Discussing the latter category, M. W. Travers[35] points out that a vitrified pot is not corroded by glass, whilst a pot in the biscuit condition is rapidly attacked at temperatures above 1200° C. It is suggested that in modern gas-fired furnace practice, the empty pot should be completely enclosed in the furnace and heated to 1350° C. until the pot material is completely vitrified and a deep skin of sillimanite has been formed. This treatment renders glazing of the pot unnecessary. Insufficient preliminary burning in the pot-arch, before the setting of the pot, is a frequent cause of pot failure, owing to differential contractions being set up in the early stages of the pot's life in the furnace.[36] A. V. Bleininger,[37] referring more particularly to pots used for melting optical glass, points out that the three main desiderata are (1) high refractoriness and capability of withstanding the hydrostatic pressure of the molten glass, (2) resistance to corrosion by the batch-materials and molten metal, and (3) freedom from iron and other colouring agents. Experiments were made with pots approaching the type of hard porcelain, and successful results obtained with the following mixture : kaolin, 25% ; felspar, 7% ; plastic bond clay, 25% ; and 43% of a " calcine " made by firing to cone 14 a mixture of kaolin, 80% ; flint, 10% ; and felspar, 10%. The waste bisque of white-ware potteries is suggested as an efficient substitute for the " calcine." Good results have been obtained by casting pots from a mixture similar to the above, the casting-slip containing 80% of solids and 20% of water, with an amount of electrolyte equal to 0·20% of the weight of the dry material.

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[32] *Trans. Ceram. Soc.*, 1918, **17**, 340.

[33] *Trans. Ceram. Soc.*, 1918, **17**, 248; *J.*, 1918, 699A.

[34] *Trans. Ceram. Soc.*, 1918, **17**, 291.

[35] *J. Soc. Glass Tech.*, 1918, **2**, 170; *J.*, 1918, 692A *J.*, 1918, 235T.

H. G. Schurecht [38] points out that to maintain a minimum viscosity in clay slips, it is more important to keep constant the ratio of electrolyte to clay than that of electrolyte to water. The experimental results confirm A. V. Bleininger's observation [39] that sodium silicate and sodium hydroxide are more effective and have a longer range of action as flocculents than sodium carbonate.[40]

Silica Refractories.—In view of the industrial importance of sands it is remarkable that, until recently, there has been little or no systematic investigation of our native resources of them. War-time conditions made it imperative to replace by home supplies the imported Continental sands which had been largely used in both the metallurgical and glass industries. The successful utilisation of British sands is, in a great measure, due to the survey of them and the investigation of their properties made by P. G. H. Boswell. In the memoir on British resources of sands suitable for furnace and foundry purposes, Boswell,[41] in addition to the field work, records much laboratory work (carried out with the assistance of Harwood and Eldridge) on the chemical, mineralogical, and mechanical composition of the sands. The essential property of a good moulding-sand lies in its water-carrying capacity; and in many of the sands which are used, this ability to absorb water without becoming really wet is due to the presence of a thin film of ferric oxide round each individual quartz grain. The general practice in this country is to use naturally bonded moulding-sands; but in America the tendency is to rely on synthetic moulding-sands made by mixing high-silica sands with clays or other bonding materials. In view of the intimate relation between fettling-shop costs and satisfactory moulding-sands it is of extreme importance that the properties of sands and the bearing of these properties on the production of clean, sound castings should be thoroughly investigated.

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[36] See S. N. Jenkinson and P. Marson, *J. Soc. Glass. Tech.*, 1918, 2, 175 ; *J.*, 1918, 692A.

[37] *J. Amer. Ceram. Soc.*, 1918, 1, 15 ; *J.*, 1918, 582A.

[38] *Trans. Amer. Ceram. Soc.*, 1917, 19, 460 ; *J.*, 1918, 508A.

[39] *J.*, 1915, 906.

[40] See also *J. Amer. Ceram. Soc.*, 1918, 1, 201.

[41] *A Memoir on British Resources of Refractory Sands.*" By P. G. H. Boswell.

The sixth volume of the 'Special Reports on the Mineral Resources of Great Britain,' by H.M. Geological Survey, deals with silicious rocks used in the making of silica bricks and ground ganister, and with the sands suitable for use in open-hearth steel furnaces. Details are given of the geological age and mode of occurrence of the rocks and sands, the method of working, facilities for transport, probable resources, &c. The absence of analyses, and other details of the laboratory work, however, militates seriously against the value of the reports, and the succeeding volume, in which this information is promised, must be awaited before they can be put to real service. It is distinctly unfortunate that it was not found possible to give the complete information, so that the reports could have been more readily utilised during the period of extreme shortage of these raw materials.

Much valuable work on silica bricks has during the year emanated from French laboratories. A. Bigot[42] further confirms the experimental results of Le Chatelier and Bogitch, and Philippon, and the advantage of the use in a silica brick mixture of a proportion of impalpable quartz powder is now fully demonstrated. The consideration of this principle is a matter which cannot be too strongly urged on English makers of silica bricks. The durability of the bricks at high temperatures is much increased by the formation of a more refractory magma and in it a network of recrystallised silica—effects which are more readily realised when the ordinary fortuitous fine material in the brick is replaced by the impalpable product of a tube-mill. A good deal of the discussion on the manufacture of silica bricks has centred round the question as to how far it is desirable, by long-continued high-temperature burning, to secure the conversion of the quartz into the forms of silica of lower specific gravity. The physical or mechanical properties of a brick may be so improved by this transformation that any method which promises to lead more easily to the desired result warrants the most careful examination and attention. The extent to which the burning of a brick can be carried must, however, remain to a considerable extent an economic question. J. S. McDowell,[43] from experimental evidence obtained in the repeated burning of bricks made from Medina quartzite, considers that to convert the whole of the quartz completely would necessitate sixteen or seventeen burnings, or one continuous burning for a month; the cost of this would obviously be prohibitive. Bricks made from fine-grained American quartzites, with a cement of amorphous silica, inverted more readily than those made from coarse-textured quartzites—an experience which confirms the comparative behaviour of British quartzites. The importance of this lies in the deduction that for a given expenditure of fuel a larger proportion of the quartz can be converted in the fine-grained cemented quartzites (such, for instance, as the Sheffield district ganister) than in the coarser-grained quartzose rocks. D. W. Ross[44] suggests that the amount of conversion obtained may be measured by a determination of the specific gravity of the brick, raw quartzites having a specific gravity of 2·59–2·66; tridymite, 2·27; and cristobalite, 2·33. An interesting development in the manufacture of silica bricks in France is the successful use of tunnel-kilns. The most satisfactory size of the type in use gives an output of 70,000 to 80,000 bricks per week. Bigot, in an earlier paper,[45] discusses the necessary qualities in the raw materials for silica brick-making, and suggests that the suitability of a quartzose material may be tested by heating it for one hour at 1710° C., all samples which do not retain their compactness and toughness being rejected. Some of the materials, however, which fail under this test may be utilised in the form of impalpable powder. For obtaining the crushed rock for the coarser portions of the brick it is not altogether desirable to use edge-runner mills as they tend to produce rounded fragments. Ideas as to the necessary freedom from ferruginous impurities of quartzose materials may require considerable readjustment as a result of the critical study of the influence of iron oxide on the properties of a silica brick containing it. A silica brick which has been used in the crown of a steel furnace can be divided into four distinct zones: (*a*) a grey portion, which has been exposed to the furnace and in which the quartz has been completely transformed into silica glass, tridymite, and cristobalite; (*b*) a hard darker portion, in which the silica is in the form of tridymite; (*c*) a transition zone of brown colour, containing some unconverted quartz, but with a dark matrix beginning to accumulate, from which the quartz will recrystallise; (*d*) a zone of unchanged brick. C. Johns, a year or two ago,[46] pointed out that from the darker portion of a silica brick, which had been in use in an open-hearth furnace, up to 15% of magnetic oxide of iron could be removed. Fe_3O_4 is the stable oxide at high temperatures, and does not combine with silica or form a solid solution. If the brick be subjected to a reducing atmosphere some fusible ferrous orthosilicate (fayalite) may be formed. O. Rengade,[47] H. Le Chatelier, and B. Bogitch,[48] and A. Scott,[49] have further examined these different zones. Zone *a* contains less basic oxides than the zones further removed from the furnace. Zone *b* is much richer in iron oxide than zone *a*, the iron oxide having penetrated between the crystals of tridymite by capillarity. A briquette cut from this region showed a contraction of 5% on heating for one hour to a temperature of 1600° C.; whereas the original brick showed an expansion under the same conditions. The contraction (due to fusion of the fluxes) is readily observed, and by faulty management of the furnace in the early stages of this seasoning process complete fusion and destruction of the brick may occur. Zone *c* contains more lime than zones *a* and *b*, and than the unused brick: the fusible silicates, or alumino-silicates of lime, having risen by capillarity, in advance of the ferruginous slag. This zone, consequently, is more fusible than the other zones, but under normal furnace conditions is protected by the more refractory zones nearer the exposed surface. This zone is also frequently fissured by the mechanical action due to the α to β quartz reversible inversion. On heating to 1600° a piece of the ferruginous zone *b*, on which was placed a similar piece of unused brick, penetration of iron oxide to a depth of 5 mm. was observed in the upper piece. Zones *a* and *b* have a considerably increased crushing strength. M. Bied[50] has shown that the addition of 5% of oxide of iron to a silica brick mixture did not appreciably lower the refractoriness of the bricks. In the absence of lime, the presence of the iron oxide apparently did not influence the formation of tridymite; but in a brick with 3% of iron oxide and 1% of lime, which was exposed in an acid steel furnace, the quartz grains completely disappeared in a few days. It is fairly evident from this work that a ferruginous quartzite can be a quite satisfactory raw material for silica brick-making. W. J. Rees,[51] in discussing the properties desirable in silica bricks for glass-works use, refers to the bleaching action of lime on bricks made from materials containing iron, it being suggested that a colourless silicate of lime and iron is formed. It is suggested, therefore, that, contrary to prevailing ideas, colour can be no criterion of refractoriness, as a white brick with high lime contents will be less refractory than a redder brick with lower lime contents. A brick of uniform texture, with no fragments larger than ¼ inch, is considered desirable for the crowns of glass furnaces, as by the increased compactness the penetration of alkaline vapours is much reduced.

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[42] Ceram. Soc., Refractories Sect., Oct., 1918; *J.*, 1918, 695A.

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[43] *Eng. and Min. J.*, 1918, **105**, 954; *J.*, 1918, 417A.

[44] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 83; *J.*, 1918, 310A.

[45] *Trans. Ceram. Soc.*, 1918, **19**, 259; *J.*, 1918, 335A.

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[46] *Trans. Faraday Soc.*, 1917, 12, 81.
[47] *Comptes rend.*, 1918, 166, 779; *J.*, 1918, 372A.
[48] *Comptes rend.*, 1918, 166, 764; *J.*, 1918, 392A.
[49] *Trans. Ceram. Soc.*, 1918, 17, 467; *J.*, 1918, 695A.
[50] *Comptes rend.*, 1918, 166, 776; *J.*, 1918, 372A.
[51] Soc. Glass Tech., Nov. 21, 1918.

Scott has further added to the evidence that tridymite is the stable high-temperature form of silica. A piece of brick which contained only tridymite, was kept at 1530° C. for two weeks, and was then quenched. So far as could be observed, the tridymite was unchanged. Where cristobalite occurs, its production can generally be traced to precipitation from molten material, and it seems probable that it develops during cooling. Prolonged annealing at 1400° C. of a portion of a brick, which when cold contained well-developed skeletons of cristobalite, followed by quenching, showed that these skeletons had redissolved to some extent, but the tridymite was unaltered.[52] J. B. Ferguson and H. E. Merwin,[53] however, in determining the melting-points of cristobalite and tridymite, have obtained results which apparently confirm the earlier observations of Fenner [54]—that the region of stability of cristobalite is above that of tridymite. On heating clear quartz crystals for 144 hours at temperatures ranging from 1300° to 1400° C., the greater part of the material was inverted to cristobalite with a few clear nuclei of tridymite. These were separated, and the melting-points determined : a new type of electric furnace, constructed on the cascade principle being used. The cristobalite melted at 1710° ± 10° C., and the tridymite grains inverted into cristobalite at 1667°–1677° C. without melting. Natural tridymites, from Nevada and Mexico, melted sharply at 1670° ± 10° C.

The explanation of these divergent experimental results must lie in the differing conditions. The presence of fluxes, which facilitate the solution and recrystallisation of the silica, brings new factors into operation which apparently have a disturbing influence on the stability ranges of the two high-temperature crystalline forms. According to Fenner, on heating tridymite with a flux (sodium tungstate) at 1470° it inverts to cristobalite. This may be due to the circumstance that above 1470° C. tridymite is appreciably soluble in sodium tungstate, the portion which dissolves being reprecipitated as cristobalite. In the bricks, calcium iron silicates and calcium aluminium silicates are the solvents, and the heat treatment is much more prolonged than in laboratory experiments, resulting in the reconversion of the cristobalite to tridymite. The cristobalite may thus be an unstable intermediate phase, crystallising from the molten magma, but finally inverting to tridymite. A. Scott,[55] and others, have shown that where cristobalite does occur in bricks heated to 1600° C. for long periods, it is invariably found in the glassy matrix or along the margins of tridymite grains in contact with it. This matrix will probably be appreciably fluid at 1500°–1600° C., and will exercise a solvent action on the tridymite, the dissolved portion being precipitated from the glassy matrix as cristobalite on final cooling of the brick. On isolated crystals the melting-point evidence confirms Fenner's interpretation; but on crystals in contact with various fluxes, the evidence and interpretations are so conflicting that further carefully controlled experimental work is obviously necessary.

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[52] *Trans. Ceram. Soc.*, 1918, 17, 459 ; *J.*, 1918, 695A.

[53] *Amer. J. Soc.*, 1918, 46, 417 ; *J.*, 1918, 546A.

[54] *J.*, 1913, 22 ; *Amer. J. Soc.*, 1908, 36, 331.

A. Scott[56] gives useful details for applying the method of Rosiwal[57] to the estimation of the proportions of quartz, tridymite, &c., in silica bricks. The method is based on Sorby's,[58] linear measurements being used instead of areal, the intercepts which the particles of each constituent make with a number of arbitrary lines being measured. Owing to the fineness of the grains of tridymite and cristobalite, it is difficult to measure more than one constituent of a silica brick, but excellent results in the estimation of the proportion of unconverted quartz have been obtained.

H. H. Thomas[59] applies the methods of Becke and Schröder van der Kolk to the identification of the various forms of silica. The latter method is easier of application and is a very sensitive one. It consists in viewing, on a dark ground, fragments of minerals placed in a liquid of approximately their own refractive index, and illuminated below by oblique white light from all sides. A solution of mercury potassium iodide in water is diluted until its refractive index for sodium light is 1·477, and a little of the powdered brick placed in it. Any tridymite (ref. index 1·477) will show ultramarine fringes; cristobalite (ref. index 1·484), orange fringes; whilst quartz (ref. index 1·549) will be fringed with white light.

The investigations of A. L. Feild and P. H. Royster[60] into the temperature-viscosity relations of the system lime-alumina-silica are of interest in their bearing on the behaviour of the matrix or

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[55] *Trans. Ceram. Soc.*, 1918, **17**, 148; *J.*, 1918, 206A.

[56] *Trans. Ceram. Soc.*, 1918, **17**, 188; *J.*, 1918, 207A.

[57] *Verhand. geol. Reichsanstalt*, 1898, 143.

[58] *Phil. Mag.*, XI., Fourth Series, 20.

[59] *Trans. Ceram. Soc.*, 1918, **17**, 311; see *J.*, 1918, 694A.

[60] *U.S. Bureau of Mines, Tech. Paper*, 189, 1918; *J.*, 1918, 548A.

"bond" of silica bricks. The greater the viscosity of the matrix at high temperatures, the stronger and more resistant to compressive stresses will the brick be. There are difficulties in the way of completely separating the matrix from the remainder of the brick, but a comparison of matrix composition with the refractoriness of the brick under load would furnish results of considerable interest.

Magnesite.—T. Crook[61] has exhaustively reviewed the known resources of magnesite throughout the world, and gives valuable details of the chemical and mineralogical composition, and of the behaviour on burning, of the different occurrences. Breunnerite, the variety of magnesite from which the Austrian magnesite bricks are made, contains a variable percentage of ferrous carbonate in isomorphous admixture. A great deal of work has been done on the utilisation of the supplies of purer compact magnesite (such as the Grecian and Italian) in the manufacture of sintered magnesia and magnesite bricks; and although during the last four years very material advances have been made in the quality of the bricks produced from these comparatively pure raw materials, there is no doubt that many users would still prefer the Styrian products. The finished product, whether sinter or brick, should consist essentially of crystalline magnesia (of the periclase family), and the formation of this is facilitated by the impurities in the Styrian raw material. The temperature required for sintering Styrian magnesite is from 1400° to 1500° C.; but to sinter Grecian magnesite much higher temperatures are necessary. The efforts to make a satisfactory product from the Grecian type magnesite have been mainly in the direction of addition of materials, such as oxide of iron (or materials which give oxide of iron on calcination), and other "fluxes," which enable the shrinkage and conversion to periclase to be accomplished at temperatures and under conditions which are readily obtainable with the kilns and furnaces available. The difficulty lies in making these additions in such a form that they come into intimate contact with the crystalline particles of magnesite. Crook considers that as the available deposits of breunnerite and spathic magnesite are so much greater than those of the compact magnesites, and as the desired product can be more economically obtained from them, it is to these deposits that the smelting industries will look in the future, as they have in the past, for the large supplies of refractory magnesia they require. There are, however, now in this country large stocks of the compact magnesites, and for this reason, and for the important reason of national security, it is desirable that the technical problems involved in their efficient utilisation should be solved.

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[61] Ceram. Soc., Refractories Sect., Oct., 1918; *J.*, 1918, 696A.

W. Donald[62] has compared the Austrian products with those obtained from Grecian magnesite. A series of synthetic mixtures of iron oxide, alumina, and silica, in the proportions in which they occur in thirteen different makes of magnesite bricks, had temperatures of incipient fusion all in the neighbourhood of 1100° C.; and mixtures made from the assumed addition of up to 9% of iron oxide to Grecian magnesite gave similar results. In discussing the influence of these impurities on the sintering temperature it is pointed out that in Grecian magnesites the magnesium silicates are much more bulky and viscous, and are not in such intimate contact with the particles of magnesia as in the Styrian magnesite. It is suggested that by the proper addition of ferrous oxide, or manganese oxide, to the Grecian magnesite, and burning the mixture at a high temperature in a reducing atmosphere (preferably in some form of rotary kiln), adequate conversion of the magnesia could be obtained and definite mineral compounds of great stability and density formed. In recent consignments of sintered Grecian material, material which, it is stated, had been burned at temperatures of over 1700° C. in gas-fired shaft-kilns[63] shows a much more nearly complete formation of the crystalline magnesia; and bricks made from this material, under suitable conditions of pressure and burning, are giving excellent results. Electric-furnace sintering or fusing may overcome many of the difficulties encountered in obtaining a satisfactory product from the present magnesites. A. Scott[64] shows that magnesite bricks have two well-defined types of structure. In the first type there are sharply defined polygonal crystals of reddish periclase in association with an unidentified isomorphous iron compound, giving to the crystals a cubic cleavage. There are also inclusions of dark crystals of magnesioferrite ($MgFe_2O_4$). Structures of this type are found in bricks having iron oxide as the main impurity. In the second type, small rounded crystals of periclase are embedded in a matrix which is generally crystalline and has a fairly low melting-point. The polygonal structure of the first type is absent, and enclosures of magnesio-ferrite are rare. It is suggested that the crystals occurring in the matrix are monticellite and forsterite. Structures of this type occur in bricks containing appreciable quantities of lime and silica. Some bricks contain both types of structure; but the first type is the more valuable as the silicate matrix in the second type is too fusible an ingredient, and is therefore undesirable. In both types it is evident that the formation of crystalline magnesia (periclase or β-magnesia) is facilitated by the impurities present.

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[62] *Trans. Ceram. Soc.*, 1918, **17**, 486; *J.*, 1918, 697A.

[63] See Steiger, *Trans. Ceram. Soc.*, 1918, **17**, 250; *J.*, 1918, 335A.

[64] *Trans. Ceram. Soc.*, 1918, **17**, 475; *J.*, 1918, 697A.

G. A. Rankin and H. E. Merwin[65] have investigated thermally and microscopically the ternary system magnesia-alumina-silica. The following crystalline substances are shown to be stable in contact with the liquid phase : periclase (MgO), corundum (Al_2O_3), tridymite (SiO_2), forsterite ($2MgO.SiO_2$), clinoenstatite ($MgO.SiO_2$), spinel ($MgO.\ Al_2O_3$), sillimanite ($Al_2O_3.\ SiO_2$), and a ternary silicate $2MgO\ 2Al_2O_3.\ 5SiO_2$ (probably an end member of the cordierite series), which is unstable at its melting-point and is considerably affected by solid solution.

Efforts have been made to replace magnesite bricks by dolomite bricks, but, so far, with little success, as their durability has been, by comparison, much less. There are abundant supplies of dolomite in this country, and numerous attempts have been made to remedy the absence of any native resources of magnesite by the decalcification of this dolomite. A chemical method of separation would be too costly. J. W. Mellor[66] suggests that advantage might be taken of the difference in the densities of the two constituent minerals when calcined at a high temperature, or of the greater inertness of the magnesite when the calcined mass is exposed to water or water vapour. This latter method was the subject of a patent taken out some years ago,[67] but the separation could, apparently, not be effected to a sufficient degree. C. Edwards and A. Rigby[68] have determined the rate of hydration of dolomite calcined at various temperatures between 850° and 1750° C. The samples calcined at 1150° C. and above, hydrated rapidly until about 20% of water had been absorbed, but beyond this point more slowly. The results obtained suggest that at first the lime hydrates fairly quickly, and that afterwards the magnesia hydrates comparatively slowly.

Zirconia.—The efforts to utilise zirconia as a high-grade refractory have, so far, not met with the anticipated success: mainly because of its undesirable tendency at high temperatures, in the presence of nitrogen or carbon, to become converted into nitride or carbide. When these difficulties are surmounted, the demand for a refractory with superior properties will be well on the way to satisfaction. It is probable that electrical fusion of the pure oxide will provide the most suitable method for industrial use; but the technical difficulties in the large-scale production of this material are not yet surmounted. There would in all probability be a considerable demand for fused zirconia, as also for fused lime, alumina, and magnesia ; so that there is an incentive for the further study of their economical production. E. H. Rodd[69] has usefully summarised the refractory properties of zirconia, and refers to its low coefficient of expansion ($8{\cdot}4 \times 10^{-7}$), by virtue of which it will resist abrupt changes of temperature. Pure precipitated zirconia is now obtainable on the commercial scale; in view of the difficulty of completely separating iron from zirconia by any economical chemical method this is a decided achievement.

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[65] *Amer. J. Sci.*, 1918, **45**, 301 ; *J.*, 1918, 300A.

[66] *Trans. Ceram. Soc.*, 1918, **17**, 119 ; *J.*, 1918, 205A.

[67] Eng. Pat. 1425, 1907.

[68] *Trans. Ceram. Soc.*, 1918, **17**, 116 ; *J.*, 1918, 209A.

[69] *J.*, 1918, 213R.

Bauxite.—N. Lecesne[70] has developed a method for the production of fused bauxite on the commercial scale. It consists in heating, in a form of cupola, a mixture of bauxite and anthracite. At the high temperature attained on applying a blast a large proportion of the impurities is vaporised. The product is useful both as a refractory and as an abrasive—the latter more particularly when ferruginous bauxites are used.

[70] *Trans. Ceram. Soc.*, 1918, **17,** 192; see Fr. Pat. 471513, *J.*, 1915, 356; also A. Bigot, *Trans. Ceram. Soc.*, 1918, **17,** 267; *J.*, 1918, 335A.

METALLURGY OF IRON AND STEEL.

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The most striking feature in the development of the iron and steel industry during the past year has undoubtedly been the adaptation and modification of plant for the recovery of potash from blast-furnace gases. It is estimated that plants are in hand and in course of erection capable of producing 20,000 tons of potash per annum, and the great freedom from dust which will result in the treated gases will greatly enhance their value and efficiency as sources of heat or power. Much attention has necessarily had to be given to the raw materials used in the industry, including the preparation of ores for smelting, the selection and preparation of refractory materials, and the economy of fuel.

Great progress has been made in the manufacture of the ferro-alloys used in the manufacture of alloy steels, especially tool steels, and the great development that has taken place in the production of machine tools has naturally been accompanied by a large amount of research work in connection with the properties and heat treatment of tool steels.

Production of Iron.

The present knowledge and practice in regard to the briquetting of iron ores is summarised by G. Barrett[1] and T. B. Rogerson, and although nothing strikingly original is included in the report, it is a useful résumé of the available information and contains a bibliography of recent literature on this important subject. It is pointed out that the product of any process should as far as possible fulfil the following conditions: It must not break into dust when dropped on a hard surface from a height of at least 10 feet; it must resist a temperature of about 900° to 1000° C. without disintegrating; it must resist the effects of the weather for a reasonable time; it must resist the action of such steam as is found in the top of a blast-furnace; it must be porous, to facilitate the penetration of the carbon monoxide of the furnace gases. The binder, if any be used, must contain no objectionable constituent, and the quantity must not seriously affect the iron content of the furnace charge, including both the ore and the limestone. The cost of production must not exceed the difference between the cost of the raw material and the value of the improved product.

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[1] *J. Iron and Steel Inst.*, 1917, **96**, 7; *J.*, 1917, 1095.

The processes in use at the present time are divided into four classes, and details are given of the most widely used methods in each class. The following are the classes given:—

1. Those in which the ore is submitted in suitable moulds to pressure high enough to cause mechanical cohesion.
2. Those in which the ore is pressed, with or without the addition of a binding agent, and subsequently heated by more or less direct firing to the temperature of incipient fusion or vitrification.
3. Those in which the ore is mixed with a binder, pressed in moulds, and hardened in air, steam, or gas.
4. Those in which the ore is heated, without pressing, to the temperature of incipient fusion or vitrification.

In view of the acknowledged necessity for increased production, the first report of Committee No. 2 of the Iron and Steel Institute[1] on blast-furnace practice is of considerable importance. It deals with an inquiry on blast-furnace practice in the United Kingdom, and summarises the answers received from twenty-six firms to a series of fourteen questions which were circulated. The subjects are as follows: (I.) The effect of the mechanical and chemical conditions of the raw materials on furnace working. Cleveland ironstone is uniform and is used in lumps as mined. Lincolnshire, Northamptonshire, and Midland ores and hæmatite vary from lumps to fine. The general practice is not to break the ore, but in the case of hard magnetite ores these are broken to about road-metal size with advantage. Durham coke, owing to its great hardness, comes to the furnaces in a more uniform condition than the softer Midland and South Yorkshire cokes, and it is generally found that with smaller makes soft cokes are used. Limestone is not generally broken below 8 in., although in some cases it is broken to 4-in. cubes. The universal opinion is that variations in yield and efficiency are directly traceable to variations in the mechanical conditions of the burden. (II.) Influence on furnace working of the dimensions of the bell relative to the stock line. Generally speaking, it is considered that the area of the bell should be about half the area of the furnace throat at the stock line. There is a considerable variation in opinion on the questions dealing with the use of double bells, the size and quality of firebricks, and the use of gas for calcining limestone.

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[1] *J. Iron and Steel Inst.*, 1918, **97**, 47; *J.*, 1918, **303A**.

The properties of coke as a fuel for blast-furnaces have been discussed by G. W. Hewson,[3] who states that the physical condition is no less important than the chemical composition. The most important physical characteristic is the hardness, which is the measure of its resistance to abrasion or crumbling. The method of determining hardness used by the author consists of placing 28 lb. of dried coke, ½ in. to 1 in. in size, in a drum or rattler 26 in. in diameter and 16 in. deep, together with a dozen cast iron balls, 1½ in. diameter. The drum is given 1000 revolutions in 1 hour and the coke is withdrawn and sieved on an ⅛-in. sieve. The percentage remaining on the sieve is taken as the hardness number. The chemical analysis and hardness numbers of a number of beehive and by-product oven cokes are given, of which the hardness numbers vary from 91·7 to 97·5. Cokes with hardness numbers below 94 are found to cause serious trouble in working. The importance of coke hardness in blast-furnace work is also dealt with by G. D. Cochrane,[4] who lays down as an axiom that " The practical success of the working of a blast-furnace is chiefly dependent on the mechanical condition of the coke used." A somewhat similar method for determining hardness to that described by Hewson is given, and comparative figures for the two methods of testing are included.

The question of fuel economy in blast-furnaces is also dealt with by T. C. Hutchinson,[5] who points out the importance of effectually cleaning the ironstone and obtaining equal distribution and admixture of the ore, coke, and limestone in the furnace itself. This latter is largely affected by the size of the bell, and with a bell of correct size the length of life of the linings is increased.

A device for cleaning, drying, and preheating blast-furnace gas is described by J. Ruddiman.[6] In the preheater hot unscrubbed gas from the furnace passes down through flues, imparting its heat to the scrubbed gas, which is conducted through a series of tubes. The preheater may act as a dust-catcher also, or a primary dust-catcher may be used. From the preheater, the unscrubbed gas passes to a primary scrubber, which consists of a series of perforated rotating baffle-plates, half submerged in water. The gas is further scrubbed in a tower containing a central rotating vertical shaft on which is arranged a series of baffles. The cool, scrubbed gas passes back into the series of pipes in the preheater and thence through a brick-lined stove main to the burners.

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[3] *J.*, 1918, 60T.

[4] *J. Iron and Steel Inst.*, 1918, **97**, 141; *J.*, 1918, 304A.

[5] *J. Iron and Steel Inst.*, 1918, **97**, 127; *J.*, 1918, 304A.

[6] *Met. and Chem. Eng.*, 1917, **17**, 608; *J.*, 1918, 32A.

Interest has been stimulated in the Cottrell precipitation process for the cleaning of blast-furnace gases by the fact that the dust often contains compounds of zinc, lead, manganese, and potash, which may be of commercial value. H. D. Egbert[7] has described the principles of the process and also some of the plants which have been put into operation.

A considerable amount of attention has been given to the recovery of potash from blast-furnace gases, and the results of analysis of various samples obtained from plants in Scotland are given by R. A. Berry and D. N. McArthur.[8] In nine samples of flue-dust, the water-soluble potash varied from 4 to 19%. The highest yield of flue-dust from coal-fed furnaces was 21 tons, but one plant using coke fuel gave a yield of 300 tons, due to higher blast pressure and absence of tarry matter; the potash content of this dust was only 3%. In three samples of stove-dust, the water-soluble potash varied from 6 to 8%; except in the case of the plant using coke fuel, the yields were negligible, and in this special case the yield was 150 tons per annum, containing 13·6% total potash, 7·6% soluble potash. Samples of tube cleanings from fifteen works were examined. These were black and contained a considerable amount of carbonaceous matter; the percentage of ash varied from 53 to 74, and this ash contained only small quantities of water-soluble potash, the highest being 2·7%. The value of these dusts, however, is high in comparison with other dusts on account of the large quantities produced annually, as, according to estimates, nearly 15,000 tons is produced from the Scottish furnaces. Samples of spent liquor were examined from fifteen works. Results are given showing the specific gravity, total solids, ash, and water-soluble potash in the ash. The specific gravity varied from 1·013 to 1·039, but one sample had a specific gravity of 1·320; with this exception, the amount of ash varied from 1·59 to 84·52 grams per gallon, and the average percentage of water-soluble potash was 33·5.

Considering that such relatively small quantities of potash are recoverable in the dust, &c., the question of the balance-sheet of potash charged into the furnace and amount capable of being accounted for is important, and the following balance-sheet for one of the plants is given:

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[7] *Blast-Furnace and Steel Plant*, 1918, **6**, 39.

[8] *J.*, 1918, 1T.

Total potash charged into furnace	7·6	lb. per ton of pig iron.
Potash accounted for:		
In spent liquor	1·40	lb. per ton of pig iron.
In flue and stove-dust	0·04	,, ,,
In pitch	1·70	,, ,,
In tube cleanings	0·20	,, ,,
In slag	2·70	,, ,,
Total	6·04	,, ,,
Unaccounted for	1·56	,, ,,

The most economical method for recovering the potash charged into blast-furnaces making ordinary pig iron is by the addition of an alkali chloride such as common salt, and in connection with the prospects of founding a potash industry in this country, K. M. Chance[9] deals largely with the recovery of potash from flue-dust, &c., obtained from blast-furnaces. The history of the preliminary investigations is given, and the value of the additions of salt to the furnace charge is shown. With regard to the costs of the process, it is pointed out that the cost of cleaning the gas must be debited to the cost of the pig iron, and the cost of raw material at the blast-furnace is therefore limited to the cost of salt, of which about 3 tons is required for 4 tons of potash in the dust. For purposes of comparison with pre-war figures, £1 per ton of salt delivered to the furnaces, or 15*s.* per ton of potash, should be ample allowance. For carriage of the dust to a central factory for treatment, 5*s.* per ton of dust, or 12*s.* per ton of potash, should suffice. The cost of potash in the raw material delivered to the factory may therefore be estimated at 27*s.* (say 30*s.*) per ton. It is pointed out that the value of the clean gas obtained from the furnaces is sufficiently great to provide a handsome remuneration for the capital expenditure and cost of operating the cleaning plant.

Reports on the present position of the malleable castings industry by W. H. Hatfield[10] and on practice in the manufacture of malleable cast iron by E. Adamson and J. E. Fletcher,[11] prepared for the Committee of the Iron and Steel Institute on Foundry Practice, have been published. The former deals with available raw materials;

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[9] *J.*, 1918, 222T.

[10] *J. Iron and Steel Inst.*, 1917, **96**, 307.

[11] *Ibid.*, 1917, **96**, 327.

the refining of irons; melting furnaces, including crucible, cupola, Siemens, and air furnaces; annealing furnaces; range of analysis permissible in malleable castings production; influence of different elements: packing materials and soundness of castings. A list of some of the scientific papers of interest to malleable founders is also added. In accepting this report, the Committee agreed to recommend that the basis of the preparation of standard pig irons suitable for the manufacture of malleable castings should be chemical analysis. They also recommend that the following two analyses of pig iron be taken as the basis specification:

		%		%
Carbon .	Minimum	3·00	Minimum	3·00
Silicon . .	,,	0·50 to 0·75	,,	0·75 to 1·00
Manganese .	Maximum	0·30	Maximum	0·30
Phosphorus .	,,	0·15	,,	0·15
Sulphur .	,,	0·25	,,	0·25

The second report deals with melting furnaces, pig iron, castings, and annealing. The following are given as the principles of annealing: (1) The higher the total carbon and silicon and the lower the sulphur and manganese, the lower will be the necessary annealing temperatures. (2) The higher the silicon and the lower the sulphur and manganese, the shorter will be the time required for annealing at given temperatures. (3) Separation of graphite can be induced at a high temperature and continued at a lower temperature. (4) The annealing temperatures recommended in America are 677° – 760° C., whilst British practice is about 160° – 200° C. above this. (5) It is the general experience in malleable castings that the lower the annealing temperature, the better the castings. A number of problems suitable for investigation are given on which there is no published information.

With a view to ascertaining to what extent a poorer class of iron could be employed for making malleable castings, J. H. Teng[13] has examined a series of irons in which the phosphorus varied from 0·05 to 0·5%. It was found that the maximum stress, elongation, and reduction in area were lowered with increasing phosphorus, the most marked effect showing at about 0·25%. The approximate limit for commercial purposes is given as 0·2%, as the ill-effects of phosphorus are not appreciable until that figure is exceeded. The presence of a considerable amount of silicon and manganese is of more importance than the absence of sulphur with regard to successful annealing.

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[13] *J. Iron and Steel Inst.*, **1918, 98, 349**; *J.*, **1918, 624A.**

PRODUCTION OF STEEL.

A triplex method for making steel is described by T. W. Robinson[13] in which Bessemer-blown metal is first produced; this is dephosphorised in an open-hearth furnace and afterwards refined in Héroult electric furnaces. A close assembly of the various units is essential for rapid and economical practice.

The reactions taking place in the acid open-hearth process are considered in detail by F. Rogers,[14] who gives special attention to the deoxidation of the bath and deals with the action of carbon, manganese, silicon, and aluminium as deoxidisers. Consideration is also given to the conditions which must be observed in order to utilise the full advantage of the high degree of deoxidation obtained and in order to minimise the piping to which such steel is otherwise subject.

The results of an investigation on the general quality and uniformity of a cast of acid open-hearth steel are given by T. D. Morgans and F. Rogers.[15] The details given include analyses of pit samples taken immediately before casting each ingot, and of the top, middle, and bottom billet from each ingot; tensile tests and Brinell tests from the top, middle, and bottom billet from each ingot, together with the results of microscopical examination. In the case of pit samples the variations in the carbon, silicon, and phosphorus contents were negligible; in the case of sulphur and manganese, the range of variation was 0·009 and 0·110% respectively. There was found to be a fairly regular fall of sulphur and manganese during the teeming of the ingots, which occupied about twenty minutes.

Preliminary reports[16] of the metallurgical and of the mechanical sections of the Committee of the Iron and Steel Institute dealing with steel and its mechanical treatment have been published, and gave rise to considerable discussion. The report of the metallurgical section dealt with a comparison of open-hearth practice at home and abroad with a view to investigating the causes of the smaller output of steel obtained from British furnaces as compared with foreign practice. The report of the mechanical section dealt with a comparison of rolling-mill practice at home and abroad with the object of ascertaining the views of manufacturers on the causes of the smaller output in British works as compared with foreign practice.

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[13] Am. Iron and Steel Inst., May 1918; *Chem. and Met. Eng.*, 1918, **19**, 15 *J.*, 1918, 470A.

[14] *J. Iron and Steel Inst.*, 1917, **96**, 181; *J.*, 1917, 1050.

[15] *J. Iron and Steel Inst.*, 1917, **96**, 209; *J.*, 1917, 1050.

[16] *J. Iron and Steel Inst.*, 1917, **96**, 267, 287.

J. N. Kilby[17] has continued his studies of steel ingot defects, and shows that variations in casting temperatures are not so great as usually supposed. The rate of pouring, however, has a great influence on the cracking of ingots. For a 7200 lb. ingot the author considers six minutes as the correct time, and states that if cast in less than three minutes 80% of the ingots will show cracks on rolling. The effect of the composition of the slag on the properties of the steel in open-hearth practice is also dealt with, and it is shown that the addition of 8–10% of lime or 6–8% of magnesia in open-hearth slags gives a reduced content of ferrous oxide, thereby enabling the slag to remove more impurities from the steel.

The production of sound steel by lateral compression of the top portion of ingots is further discussed by B. Talbot,[18] who states that a larger percentage of solid steel, fit for commercial purposes, can be obtained if the top portion of the ingot be compressed before its centre is entirely solid, than is the case with the usual method of casting with refractory tops.

The manufacture of tinplate is described by T. Lewis Bailey,[19] details being given of the operations involved, from the cutting of the bars to the cleaning of the finished plates. The development of the tinplate trade has been essentially along mechanical lines, but there are problems which would repay chemical investigation, and this applies especially to the treatment of the dross which collects on the surface of the tinning pots.

Physical Properties, Heat-Treatment, Etc., of Iron and Steel.

An interesting study of blast-furnace bears has been carried out by J. E. Stead,[20] who has been fortunate in obtaining a large number of examples. The bears are found below the hearth level of the blast-furnace as a result of the fluxing away of the bottom linings of the furnace and replacement by metal. In the course of time the metal gradually works its way downwards for a distance of 3 to 12 feet or more, and solidifies into masses which may weigh anything between 50 and 800 tons. The bears are very variable in character, and specimens form a fertile field for metallographers. Some of the most interesting constituents of bears include spheroidal forms of graphite, accumulations of sulphides of iron and manganese, cyano-nitride of iron in red crystals, titanium dicyanide in blue crystals, masses of oxides and silicates of iron, decarburised metal, crystals of iron carbide and phosphide, and carbo-silicide of iron and manganese.

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[17] *J. Iron and Steel Inst.*, 1918, **97**, 365; *J.*, 1918, 267A.

[18] *J. Iron and Steel Inst.*, 1918, **97**, 221.

[19] *J.*, 1918, 113T.

[20] *J. Iron and Steel Inst.*, 1918, **97**, 157; *J.*, 1918, 304A.

In some notes on the heat treatment of grey cast iron for internal combustion engine cylinder components, J. E. Hurst[21] deals with the question of the behaviour of cast iron when subjected to heat, in so far as it is concerned with the deterioration of the above-mentioned parts. It is pointed out that these cylinder components, which are subjected to the direct influence of the heat, crack and become utterly useless, and this cracking is most pronounced in the cast iron piston-heads of Diesel engines. Analyses of a series of heat-treated cast iron bars are given, together with photomicrographs, and it is concluded that the ultimate cracking of Diesel engine piston-tops can as a rule be traced to the phosphorus content of the iron.

The properties of acid-resisting iron are dealt with by S. J. Tungay,[22] who shows the great advantages obtained from the use of acid-resisting materials of the nature of cast iron over brittle and friable materials such as glass, pottery, &c. The results obtained by Kowalke on the losses sustained on treatment in 10% sulphuric, nitric, and hydrochloric acids of iron containing from 2·5 to 19·8% of silicon are given. The results of corrosion tests carried out by the author on "Ironac" in stronger acids are also given. The following table gives comparative figures for ordinary cast iron and acid-resisting iron :

	Ordinary Cast Iron.	Acid-resisting Iron.
Density	7·3	6·8
Tensile strength (tons per sq. in.) .	9 to 10	6 to 7
Melting point	1150° C.	1200° C.
Hardness	24	35
Heat conductivity	10	8
Electrical resistance . . .	8	10
Contraction per ft. in casting .	$\frac{3}{32}$ in.	$\frac{9}{32}$ in.
Crushing strength (1 in. cubes) .	40 tons	34 tons

The iron alloys containing less than 10% of silicon are attacked by sulphuric, hydrochloric, acetic, and citric acids, but alloys containing from 16 to 18% of silicon are highly resistant to these acids ; the latter are extremely brittle and are so hard that high-speed abrasive wheels have to be used for grinding into shape.

The various acid-resisting alloys are compared with one another and with ferroboron and Borchers metal by C. Matignon.[23] The Borchers metal was made up to contain Ni 64·6, Cr 32·3, Ag 0·5, Mo 1·8, and the following table gives the composition of the other alloys tested:

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[21] *J. Iron and Steel Inst.*, 1917, **96**, 121 ; *J.*. 1917, 1050.

[22] *J.*, 1918, 87T.

	French.	Italian.		American.		
	Métallure.	Elianite 1.	Elianite 2.	Ironac.	Duriron.	Ferroboron.
Si . .	16·92	15·07	15·13	13·16	15·51	4·9
Fe . .	81·05	82·40	80·87	83·99	82·23	69·8
Mn . .	0·88	0·62	0·53	0·77	0·66	3·3
Ni . .	—	—	2·73	—	—	—
Al . .	0·25	—	—	—	—	3·1
C . .	0·592	—	0·82	1·08	0·83	—
P . .	0·173	—	0·06	0·78	0·57	—
S . .	0·01	—	0·03	0·05	0·01	—
B . .	—	—	—	—	—	15·4
Sp. gr.	6·71	6·87	7·14	6·71	6·94	—

The ferroboron did not resist the action of either weak or strong nitric acid. Borchers alloy was more resistant to weak nitric than to the strong acid, but it did not show any advantage over the iron-silicon alloys, which are cheaper. Métallure gave the best results, and the 2% of nickel in Elianite 2 improved this metal as compared with Elianite 1. None of the alloys resisted the action of hydrochloric acid.

The results of an examination of the microstructure of commercially pure iron between Ar_3 and Ar_2 are given by W. J. Brooke and F. F. Hunting.[24] The work was undertaken with a view of investigating the well-known phenomenon that iron of great purity produced in basic open-hearth furnaces similar to "Armco iron" is redshort when subjected to mechanical treatment between 800° and 900° C. At any temperature other than those within this range, great ductility and malleability are the prominent properties of the iron. The results indicate that within the range of temperature mentioned, a eutectoid is thrown out of solution. This eutectoid is found at the boundaries of the crystals, which tend to increase in size at these temperatures. As the temperature falls, the ferrite grains become smaller and the ferrite redissolves the eutectoid, the structure of the material regaining that of normal ferrite.

The results of the scientific research of the last twenty-five years has given us the necessary information to determine the theoretically correct heat treatment for almost any steel when dealt with in small

[23] *Comptes rend.*, 1918, **166**, 815; *J.*, 1918, 375A.

[24] *J. Iron and Steel Inst.*, 1917, **96**, 233; *J.*, 1917, 1096.

masses. The heat treatment of large masses of steel, however, presents many difficulties which do not exist in the case of small pieces, and the effect of mass action is of considerable importance. In this connection E. F. Law[25] gives the results of an investigation on the changes taking place in the interior of a mass of steel during treatment.

The results of experiments on the influence of heat treatment on the electrical and thermal resistivity and on the thermo-electric potential of some steels, including carbon steels, nickel steel, nickel-chrome steels, a silicon and a manganese steel, are given by E. D. Campbell and W. C. Drood.[26]

C. A. Edwards[27] deals with the hardening and tempering of steels, especially as regards those containing nickel, chromium, and tungsten. The importance of the initial temperature and the rate of cooling is pointed out. By carburising the surface of a 7% nickel steel originally containing 0·1% of carbon, and allowing it to cool slowly, the same effect is produced as by carburising and quenching an ordinary mild steel. In the case of a chrome steel containing 6% Cr and 0·63% C, the rate of cooling may be decreased without detriment to the hardness, provided the initial temperature is raised. Case-hardening effects may be produced in steels containing 6% Cr and 1% C by decarburising the surface to below 0·6% C.

The importance of the initial temperature and the time factor of cooling, in the heat-treatment of special tool steel containing 18% W, 3% Cr, 0·62% C, and 0·95% V, is shown by results published by M. Yatesvitch.[28]

Considerable attention has again been given to the nature of the non-metallic inclusions found in steel, and the importance of this subject is now being fully realised. It is surprising what very little definite information exists on the composition of these inclusions, and a paper by A. McCance[29] on the subject will be widely read. Inclusions are shown to be a source of weakness in stressed material. There is no evidence to support Liegler's suggestion that the non-metallic inclusions are soluble in steel, and their importance is therefore concerned with their existence as separate particles. They do not obey the laws which govern the segregation of elements such as carbon, phosphorus, &c., soluble in liquid steel; their ultimate position in the ingot being determined by secondary influences or by chance, and during the solidification of the metal they may be carried into any part by local movements and convection currents. Although lighter than the metal, the probability of minute particles rising to the surface is practically *nil.* Coalescence occurs during the solidification of the last portion of metal and this results in the inclusions becoming crowded together. The beneficial effect of manganese on steel is studied, and the author concludes that sulphide inclusions may consist of manganese sulphide, but they are not likely to contain any ferrous sulphide, even in solid solution. Manganese silicate inclusions and iron oxide scales and silicates receive attention, also open-hearth slags and fluxed refractory materials. The influence of temperature on the prevalence of inclusions is dealt with, and it is shown that they are less prevalent with hot cast metal than with cold cast metal.

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[25] *J. Iron and Steel Inst.*, 1918, **97**, 333; *J.*, 1918, 305A.

[26] *J. Iron and Steel Inst.*, 1917, **96**, 251.

[27] Manchester Association of Engineers, Feb. 9, 1918. *Engineering*, 1918, **105**, 267; *J.*, 1918, 209A.

[28] *Rev. Mét.*, 1918, **15**, 65; *J.*, 1918, 268A.

[29] *J. Iron and Steel Inst.*, 1918, **97**, 239; *J.*, 1918, 267A.

The question as to whether or not non-metallic inclusions in steel induce ferrite to crystallise round them has often arisen, and J. E. Stead[30] publishes the results of a large number of experiments to decide the point. In no case were inclusions of quartz, magnesia, lime, basic open-hearth slag, or manganese sulphide, artificially introduced into steel bars containing 0·16, 0·34, and 0·48% C, found to lead to the development of a ferrite envelope when the bar was heated to and slowly cooled from 1200° C. Fluorspar proved an exception, and mill scale and iron oxide slags wholly or partially decarburised the adjacent metal. Hermetically sealed cavities made in steel did not cause ferrite or cementite layers to form. The effect of phosphorus was shown by heating and cooling steels containing 0·07 and 0·3% P respectively. Before heating, both samples showed white bands round the non-metallic impurities, but after slow cooling from 1200° C. these were absent, due to the diffusion of the phosphorus concentrated in these bands. Pure slag inclusions do not effect a segregation of ferrite, and the presence of ferrite ghost lines is due to the presence of phosphorus. H. Brearley, however, has found that when sand was incorporated in steel which was afterwards forged down and annealed, ferrite lines appeared enveloping the inclusions.

J. E. Stead[31] has also carried further his studies of the alloys of iron, carbon, and phosphorus, the first portions of which were published in 1915.[32] It is now shown that as carbon enters into phosphorised iron by cementation, the phosphide of iron diffuses out of the areas and is concentrated in solid solution in the surrounding ferrite. The amount of carbon capable of passing into iron by cementation at any given temperature, short of the ternary eutectic formation point, depends upon the amount of phosphorus present in the iron and varies inversely with the phosphorus. With regard to the temperature ranges in which free phosphide of iron passes into and out of solution in iron, it was found that solution of phosphide in phosphorus-free iron had occurred at 700° C., but in iron practically saturated with phosphide the temperature required was higher. Conversely, observations on the temperature at which iron phosphide falls out of solid solution show that the amount present is the vital factor.

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[30] *J. Iron and Steel Inst.*, 1918, **97**, 287; *J.*, 1918, 267A.

[31] *J. Iron and Steel Inst.*, 1918, **97**, 389; *J.*, 1918, 268A.

[32] *J. Iron and Steel Inst.*, 1915, **91**, 140; *J.*, 1915, 616.

The heterogeneous structure, visible to the naked eye, in polished and etched specimens of commercial steels is attributed by H. Le Chatelier and B. Bogitch[33] to oxygen in solid solution in the steel, neither phosphorus nor sulphur having any direct influence. Electrolytic iron, with or without the addition of iron phosphide or sulphur, when melted in an atmosphere of hydrogen, was homogeneous on etching, but the same metal, if melted with excess of air or with the addition of iron oxide, showed a heterogeneous structure. If heated below its melting point, the heterogeneity only occurred in the surface layers.

The results of a research on the effects of cold-working on the elastic properties of steel are published by J. A. Van den Broek.[34] Mild steel was subjected to cold-stretching, compression, and twisting, and afterwards tested with reference to its elastic properties. Cold-stretching was not found to lower the elastic limit in compression, and the effects of cold-working are probably a function of the strains and are independent of the stresses involved in the process. When a mild steel is cold-worked and properly heat-treated the elastic limit may be raised more than 100%, when tested in the same direction as the appplied stress. Cold-working breaks up the coarser crystalline structure and planes of weakness, with the formation of amorphous metal, and after ageing, the elastic limit is not reached until a greater stress than that at which cold-working is discontinued is attained. The beneficial effect of cold-working is permanent.

The effect of cold-working of steel from another point of view has been examined by J. H. Whiteley,[35] who found that cold-working generally resulted in a higher Eggertz colour figure for combined carbon. On examining the effect of annealing after cold working on the divorce of pearlite, it was found that by annealing at 500° C. after cold-work, pearlite showed a tendency to break up, and by annealing at 680° C. the divorce was complete in less than two hours, whereas with a similar steel in an unstrained condition the pearlite was practically unchanged.

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[33] *Comptes rend.*, 1918, **167**, 472; *J.*, 1918, 701A.

[34] *Carnegie Scholarship Mem., Iron and Steel Inst.*, 1918, **9**, 125; *J.*, 1918, 267A.

[35] *J. Iron and Steel Inst.*, 1918, 97, 353; *J.*, 1918, 267A.

E. B. Wolff[36] publishes the results of a research undertaken with a view of determining the causes of the cracking of boiler plates over the riveted seams. It is shown that peculiar types of cracks occur in riveted joints of all kinds of boilers in service. These cracks are in most cases invisible in the beginning and can then only be detected after etching. They are found in lap joints and butt strap joints, in shell and front plates, as well as in firebox plates. The results of the measurement of the real stresses in different places of the riveted joints are given, and it is shown that the view held previously that these cracks have been caused by fatigue of the material is probably correct.

The cause of another case of failure of boiler plate has been investigated by W. Rosenhain;[37] in this case the failure occurred in the last stage of the manufacture of the plate. The results of the investigation indicated that the failure was the result of coarse crystal structure in carbonless bands, and that these were due to grain growth produced by slight deformation and subsequent low temperature annealing; normalising was found to remove this source of weakness.

The action of caustic liquors on steel plates has been further examined by C. E. Stromeyer,[38] and the results obtained are contained in the Annual Report of the Chief Engineer to the Manchester Association of Engineers. Evaporator tubes exposed to caustic soda liquors showed cracks where the steel had been stressed in tension, but none where it had been under compression. This observation was confirmed by experimental work on rings so arranged that some were in tension and others in compression. It was found that after exposure to caustic soda for periods up to four months, the rings which had been in tension, whether annealed or not, developed numerous cracks on deformation, whilst those which had been in compression did not. The steel probably absorbs hydrogen when in contact with caustic soda and so acquires brittleness.

The different methods in use for the cleaning of metallic surfaces and for pickling of steel sheets, &c., have received a considerable amount of attention with a view of ascertaining the most economical method under given conditions. In this connection, M. de K. Thompson and F. W. Dodson[39] have published the results of comparative experiments on the chemical and electrolytic pickling of black sheets. Electrolytic pickling was found to give a better surface than chemical pickling,

[36] *J. Iron and Steel Inst.*, 1917, **96**, 137.

[37] *J. Iron and Steel Inst.*, 1918, **97**, 313; *J.*, 1918, 305A.

[38] *Chem. Trade J.*, 1917, 533; *J.*, 1918, 60A.

[39] *Met. and Chem. Eng.*, 1917, **17**, 713; *J.*, 1918, 92A.

and the amounts of iron dissolved from the black sheets were 0·0032 and 0·00386 grm. per sq. in. of surface respectively.

J. N. Friend[40] has continued his work on the protection of iron against atmospheric corrosion by means of paint. He shows that acceleration tests are of little value, and that reliable results can only be carried out under practical conditions. Addition of pigment to oil increases the efficiency of the latter up to a maximum, after which further additions of pigment cause deterioration. Linseed oil expands on setting and this results in crumbling and cracking. The best results are obtained by multiple coats, two thin coats being found to be better than one thick one. Turpentine has little effect on the efficiency of a paint, and the most permanent paints are those containing black and red pigments, whilst fine pigments afford more efficient protection than coarse pigments. Iron should be painted while the scale is still on it; the paint will then last longer than if applied to the pickled or sand-blasted surface.

[40] *Carnegie Scholarship Mem., Iron and Steel Inst.*, 1918, **9**, 71; *J.*, 1918, 736A.

METALLURGY OF THE NON-FERROUS METALS.

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In the following review of the metallurgy of the non-ferrous metals it will be noted that no development of outstanding importance has been made public during the year. It does not follow, however, that the industry has remained stationary over the period under review, for in all probability there are new features in the experimental stage which will be made known when they reach a stage of development that will insure ultimate success.

Existing processes have been improved both in the matter of design of plant and details of working, and further economies have been made.

Attention has been drawn again to the utilisation of what are termed waste products, and in this direction there is still scope for ingenuity and research.

The output of allied countries has increased generally, on account of the increased demands created by war conditions, and there is every indication that under normal conditions no effort will be spared further to increase supplies from such sources. There is a fear, however, in certain quarters that the cessation of hostilities will result in over-production, and some attribute the fall in price of zinc to this cause. It must be remembered that the demand will steadily grow after a normal course is resumed, and until that time arrives it would be unwise to come to a conclusion on this point.

Gold and Silver.

In the metallurgy of gold it will be seen that the chief interest has centred in the precipitation of the metal from cyanide solutions, and interesting developments may be looked for both in the mode of precipitating the metal and in the precipitant employed.

With reference to plant, there has been little if any deviation from standard practice, even although the preparation of the ore for cyaniding has been modified in certain instances. Until recently the cyaniding of graphitic gold ores necessitated a preliminary roast to remove the carbonaceous matter on account of the graphite interfering with the solution of the metal. P. T. Bruhl[1] now shows that by submitting such ore to flotation, a flotation concentrate can be obtained consisting of graphite, mispickel, and auriferous pyrites, which after roasting can be added to the tailings and the product directly cyanided, as the tailings are relatively free from carbonaceous matter. This scheme greatly reduces the amount of material to be handled at the roasters, and thereby should reduce the ultimate cost.

At the Prestea mines material of the above character has to be dealt with, but F. Wartenweiler[2] shows that another method has been successful.[3] The method consists of leaching with a dilute solution of sodium sulphide after cyaniding, as it has been found that carbonaceous matter does not interfere with this solvent. The gold is recovered from the solution by using copper as a precipitant; copper is quite satisfactory for this purpose, although it is stated that an alloy composed of equal parts of aluminium and zinc will give superior results.

The leaching of roasted sulpho-telluride ores containing lime has presented difficulty in the past on account of the formation of calcium sulphate, which during leaching operations acts as a plaster and causes the pulp to set.

A. L. Blomfield and J. M. Trott[4] state that at the works of the Golden Cycle Mining and Reduction Co., Colorado Springs, the difficulty has been overcome by raising the temperature at one stage of the roast, which is conducted in Edwards' Duplex furnaces, above 870° C. According to the literature available on the subject of the dead-burning of gypsum, in which state setting and hardening do not take place or only very slowly, it appears that a lower temperature than that stated above would produce the desired result provided the material was in a sufficiently fine state of division and was heated for a sufficient length of time.

Turning now to precipitation problems, it is well known that the zinc consumption has been out of all proportion to the gold and silver precipitated, due partly to the zinc which remains with the slime, and which necessitates a slime treatment for its removal, and partly to the zinc which is dissolved in excess of the amount required to replace the metals that are precipitated. The removal of dissolved air from the solution has reduced the zinc consumption by one-half, as shown by the results obtained at the plant of the Portland Gold Mining Co., Colorado Springs.[5] It has been possible at this plant to abandon the practice of adding solid cyanide at the head of the precipitation plant, and this suggests that the saving in zinc is partly due to the fact that the elimination of the air prevents the re-solution of the gold.

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[1] *Eng. and Min. J.*, 1918, **105**, 197; *J.*, 1918, **152A**.

[2] Inst. Min. and Met., July 25, 1918, *J.*, 1918, **470A**.

[3] See *Annual Reports*, **2**, 265.

[4] *Eng. and Min. J.*, 1918, **106**, 400 *J.*, 1918, **626A**.

The use of zinc dust has not shown any real development, and it may be that this can be accounted for by the very low working efficiency on a large-scale plant. W. J. Sharwood[6] states that the efficiency may be much less than 1% in the case of weak gold solutions and as much as 50% in the case of rich silver solutions. This indicates that the efficiency is a function of the solution, but Sharwood also shows that it is affected by the purity of the zinc.

This is confirmed by R. Wheeler,[7] who advocates the use of pure zinc dust (98 to 99%), as the consumption is 30 to 40% less and the resulting bullion purer.

The use of charcoal as a precipitant has not secured much favour in the past, but the interesting and valuable account given by H. R. Edmands[8] of its application at the Yuanmi Gold Mines should do much to bring it into favour. On account of the difficulties experienced with zinc dust, charcoal was substituted in 1916 and proved quite satisfactory, inasmuch as there was an improved recovery of gold at a decreased cost. The process, which is preferably carried out in three stages, consists of filtration through charcoal cakes in Moore-Edmands vacuum filters, the cakes, when sufficiently impregnated with gold, being washed and burnt and the resulting ash melted down. It is necessary to take certain precautions in the preparation of the charcoal, and it is possible, in the light of further research, that it will be found advisable to use charcoal from particular sources. Considerable discussion has taken place on the theory of the process, and it has been suggested that the carbonyl group plays an important part in the reaction.

The increased price of silver has stimulated production of the metal, but unfortunately an artificial stimulus of this character often results in less economical working. In the case of silver-ore treatment, it is gratifying to find that recovery has not been sacrificed for production. At Pachuca and at Cobalt, for example, H. A. Megraw[9] shows that the introduction of flotation has increased the recovery and lowered the cost.

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[5] *Eng. and Min. J.*, 1918, **106**, 413; *J.*, 1918, 626A.
[6] *Met. and Chem. Eng.*, 1917, **17**, 437; *J.*, 1917, 1179.
[7] *Eng. and Min. J.*, 1918, **106**, 22; *J.*, 1918, 470A.
[8] *Trans. Inst. Min. and Met.*, 1917–18; *J.*, 1918, 183A.
[9] *Eng. and Min. J.*, 1918, **105**, 102; *J.*, 1918, 152A.

Details of present-day flotation practice as carried out in the Cobalt district are given by R. E. Dye [10] and J. M. Callow and E. B. Thornhill,[11] and from these accounts it will be seen that cyaniding still plays an important part. At present, therefore, flotation must not be considered as an alternative to cyaniding, but rather as an adjunct. With further experience it may be possible to obtain a product which will give better results if smelted than if cyanided, but even then the cyanide process will not be displaced altogether, for there are districts in which flotation has been tried without success. In connection with the combined flotation-cyanidation process, the tests carried out by J. G. Parmelee [12] are instructive. The results show that when the metals are not present as sulphides the oil used for flotation has no detrimental effect on the cyaniding operation, whereas with sulphides the oil coating acts as a protective agent and should be removed by a low-temperature roast or some other suitable method.

MERCURY.

There is little progress to report in the metallurgy of mercury, and it is difficult to obtain reliable data as to production on account of the conditions existing in 1917–18.

The past year, however, has again shown the general advantage of the Scott furnace, but it is interesting to note that the New Idria Company have installed a rotary furnace similar to the rotary cement kiln.

In the past no success has been gained in attempts to extract mercury by wet methods, but the method described by C. H. Holland [13] yields a relatively good result in regard to the amount extracted, viz. 84·5%; it is, however, probable that other economic considerations will prevent a general application of the process. The method as described consists of agitating the crushed ore with an aqueous solution containing 4% sodium sulphide and 1% sodium hydroxide and precipitating the mercury from the double sulphide by aluminium shavings. Apart from the fact that part of the mercury so obtained is in a condition which necessitates retorting with manganese dioxide and lime, it must be remembered that the aluminium losses may prove to be high on account of the alkali attack and the rapid oxidation that

[10] *Trans. Canadian Min. Inst.*, 1917, **20**, 11; *J.*, 1918, 210A.

[11] *Ibid*, 28–37; *J.*, 1918, 210A.

[12] *J. Chem. Met. and Min. Soc. S. Africa*, 1918, **18**, 165; *J.*, 1918, 210A.

[13] *New Zealand J. Sci. and Tech.*, 1918, **1**, 153; *J.*, 1918, 548A.

will occur whenever the mercury-treated metal becomes exposed to the air.

LEAD.

Smelting practice has shown no marked change during the past year, although efforts have been made to reduce the cost of production by improving the recovery and reducing labour. Considerable attention has been given to the problem of efficiently treating lead-zinc ores, and some progress has been made in the extraction of lead from this class of material.

It has always been considered that in due course a practical scheme for treating ores of the Broken Hill type would be devised, but in the past the aim has been chiefly in the direction of removing the zinc by solution, thus leaving a lead residue sufficiently low in zinc to permit of economic smelting. Recently, however, the aim has been reversed, and the leaching methods reported show that it is possible to remove the lead in solution and leave the zinc in the residue. H. O. Hofman,[14] for example, states that leaching experiments were carried out at Kellogg with good results. The ores were first subjected to a chloridising roast and then leached with acidulated brine. The yield was 85–95% of the lead and 80–90% of the silver contents.

H. L. Sulman and H. F. K. Picard[15] have patented a method for extracting lead sulphate by dissolving it in hot saturated brine and precipitating the lead by sodium carbonate or sodium sulphide. A feature of the process is the regeneration of sodium chloride from the sodium sulphate formed, by means of calcium chloride, which at the same time prevents an accumulation of the alkali sulphate.

O. C. Ralston, C. E. Williams, M. J. Udy, and G. J. Holt[16] also refer to a leaching method available for oxidised lead ores in which a saturated solution of salt acidified with sulphuric acid is used, followed by electrolytic or lime precipitation.

The volatilisation of the metal as chloride has also received considerable attention. A. E. Wells[17] gives an interesting report on the extraction of lead from low-grade ores by this method. The chloride is produced by mixing the ore with sodium chloride or calcium chloride and heating the mixture to 800° C., at which temperature lead chloride volatilises. It appears necessary to adopt the Cottrell precipitator or a similar electrical plant to obtain an efficient recovery of the fume.

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[14] *Eng. and Min. J.*, 1918, **105**, 93; *J.*, 1918, 152A.

[15] Eng. Pat. 109817; *J.*, 1917, 1181.

[16] *Met. and Chem. Eng.*, 1917, **17**, 437; *J.*, 1917, 1180.

[17] *U.S. Bureau of Mines Salt Lake Exp. Sta: Report*, 1917; *J.*, 1917, 721.

"The recovery of the lead from the chloride is accomplished by heating with a reducing agent and lime as a flux, whereby calcium chloride is produced, which can be used as stated above for chloridising further ore charges.

Provided the lead losses associated with this method of reduction are reasonably low, there is a possibility of this part of the operation being utilised generally for obtaining lead from chloride or oxychloride.

According to Ralston and his colleagues, as mentioned above, the use of calcium chloride in place of salt results in 50–75% of the chlorine being recovered.

Reverting to smelting practice, it may be mentioned here that the problem of dealing with small supplies of rich galena has been overcome in the Middle Western States and other places by smelting concentrates in mechanically operated Scotch hearths. The success of such method of working is indicated by W. E. Newnam,[18] who states that the quantity of "grey" slag formed averages only 2% of the ore, which means that the proportion of lead sent into the slag is about one-tenth the amount sent into the product obtained by the older form of hearth smelting.

COPPER.

The production of copper for 1917 and 1918 will probably be found to be as great as in 1916. At the time of writing this report the complete returns for 1917 were not available, but as regards the United States, the smelter production was very similar to that of the previous year.[19]

During the years 1912 to 1915 the quantity produced in the different countries was fairly uniform each year, and the total production amounted to approximately one million metric tons per annum, whereas in 1916, according to the U.S. Bureau of Standards,[20] the total production reached 1,396,609 metric tons.

No development of fundamental importance has taken place in the metallurgy of copper either in the preparation of the ore, the extraction of the metal, or in the refining operation. With reference to the preparation of the ore, the progress of flotation has been very considerable, and, generally speaking, in the United States the large concentrating plants now include flotation units for dealing with the fines and slimes. At one time it was considered that flotation and leaching would prove to be rival processes, but it now appears that the general trend is in the direction of these operations becoming interdependent.

[18] *Eng. and Min. J.*, 1918, **106**, 101; *J.*, 1918, 548A.

[19] *Iron and Coal Trades Review*, Aug. 2, 1918; *J.*, 1918, 365R.

[20] *U.S. Bureau of Standards, Circular No.* 73; *J.*, 1918, 358R.

In connection with the extraction of the metal by smelting, further attention has been given to furnace linings. The life of the lining of copper converters is a matter of great importance, and any practical method which would prolong the life would be of great benefit to the industry. M. W. Krejci[21] shows how the life of magnesite linings has been so improved at the Great Falls Smelter that with due care and occasional repair such linings last almost indefinitely. The method consists of coating the magnesite when in place with magnetite obtained by blowing matte for a short period without any silica addition. This discovery should have a far-reaching effect.

The revival of the use of reverberatory copper smelting furnaces has been brought about in some measure by the increasing quantity of concentrates produced by flotation. Gas-fired furnaces of large capacity are in regular operation, and any attempt to reduce the cost of smelting would be welcomed. According to F. Rutherford,[22] since 1912 the hot material from the roasters has been fed at the sides of reverberatory furnaces instead of the centre, and this variation in practice is said to have reduced the metal loss.

Dealing now with wet methods of extraction, the weathering and heap leaching of Rio Tinto ores has been practised for a very considerable period, and now, according to C. D. Van Arsdale,[23] there is every possibility of similar practice being adopted in the United States; in fact, at Tyrone, N.M., and Bisbee, Arizona, dumps of 20,000 tons and 9500 tons respectively are being treated in this manner, and with encouraging results.

The use of ammonia as a solvent has been known for a long time, but the difficulty has been chiefly in the direction of reducing the losses to a reasonable figure. The results, however, of treating tailings from the Calumet and Hecla Mining Companies' mills in a 2000-ton plant with ammonium carbonate are very encouraging, and show considerable promise. C. H. Benedict[24] states that the total cost works out at \$0·406 per ton of tailings or \$0·05 per lb. of copper, whilst the average extraction, after ninety hours' leaching, works out at about 75%, with an ammonia loss of approximately 1 lb. per ton of sand treated.

According to H. M. Lawrence,[25] an 800-ton plant is in course of construction on the Bonanza and Jumbo Mines, Alaska, for treating tailings which contain copper, chiefly in the form of carbonate. As in the case just cited, the average extraction from tests made is

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[21] *Eng. and Min. J.*, 1917, **104**, 669; *J.*, 1918, 11A.

[22] *Eng. and Min. J.*, 1918, **106**, 109; *J.*, 1918, 547A.

[23] *Eng. and Min. J.*, 1918, **105**, 225; *J.*, 1918, 183A.

[24] *Eng. and Min. J.*, 1917, **104**, 43; *J.*, 1917, 966.

[25] *Eng. and Min. J.*, 1917, **104**, 781; *J.*, 1918, 10A.

75%, but the ammonia losses are stated to be ½ lb. per ton of tailings treated.

In April 1916 a 5-ton plant was erected at Thompson, Nevada, for the treatment of oxidised copper ores. The solution obtained by leaching these ores with sulphuric acid is neutralised with lime and then treated with sulphur dioxide, after which it is heated to 160° C. under a pressure of 100 lb. E. R. Weidlein[26] states that the copper finally precipitated shows a purity of 99% after being melted.

R. Gahl[27] proposes to recover copper from dilute sulphate solutions by the use of finely divided limestone. The reaction, which is well known, would result in a product containing, under the best conditions, about 20% of copper and over 20% of lime, a considerable part of the latter being as sulphate. It is difficult to see how this product could be smelted at a low cost.

Leaching processes in which acids form the leaching solution have been practically impossible when applied to ores containing lime in a soluble form and alumina, on account of the high acid consumption and other difficulties that are encountered, but the method adopted at the Nevada Douglas Consolidated Copper Co.'s mine has proved successful.

According to G. C. Westby,[28] leaching by direct contact with roaster gases in the presence of steam and leaching liquor has given 98% extraction in forty days. The system is in a measure a counter-current system, inasmuch as the roaster gases are blown upwards by a steam jet through the leaching towers, thus meeting the leaching liquor which descends through the ore. The active agent is the sulphur dioxide, which produces a copper bisulphite, probably with some sulphate, and the copper is recovered from these compounds by passing the solution over iron. The treatment costs work out at just under $1·0 per ton.

Copper obtained by smelting or by hydrometallurgical methods must be refined, either electrolytically or by the furnace method. Refining furnaces and accessories show some progress in their development, especially in the direction of the design and construction of the furnace itself, and also the mechanical appliances for handling material before and after refining. L. Addicks[29] gives a good account of such developments, and at the same time emphasises the need of improvement in the matter of the better utilisation of labour.

Refining is all-important when the copper is to be used for the manufacture of alloys such as cartridge brass or for electrical conductors. The influence of impurities on electrical conductivity has been further studied by F. Johnson,[30] who shows that when the impurities generally present are grouped according to their physico-chemical behaviour when alloyed with copper, it is possible to deduce a reason for the differing influence. The three suggested groups are:

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[26] *J. Ind. Eng. Chem.*, 1917, **9**, 1057; *J.*, 1918, 10A.

[27] U.S. Pat. 1269418; *J.*, 1918, 551A.

[28] *Eng. and Min. J.*, 1917, **104**, 119; *J.*, 1917, 966.

[29] *Met. and Chem. Eng.*, 1917, **17**, 579; *J.*, 1918, 32A.

(1) Elements which exist as insoluble constituents, either pure metal or compound, viz. Pb and Bi (as pure metals), O, S, and Te (as compounds).

(2) Those which enter into solid solution, but not as intermetallic compounds, viz. Ag, Au, Zn, Fe, and Sn.

(3) Those which enter into solid solution as compounds, viz. Sb, Si, P, As, and Al.

The elements referred to in the first group influence the conductivity roughly proportionally to the quantity present, whilst those given in the third group produce a most marked drop in the conductivity.

Rapid methods for the determination of impurities would be advantageous in this connection. A quick method for the determination of lead in factory samples of copper, devised by C. W. Hill and G. P. Luckey,[31] gives results sufficiently reliable for practical use in the copper refinery. The method involves the use of the spectroscope, and it is stated that with a carefully regulated arc the time required to cause the disappearance of the bright lead line in the spectrum varies regularly with the amount of copper used and with the percentage of lead present.

ZINC.

In the zinc industry the outstanding features are connected with roasting furnaces, the utilisation of roaster gases, the application of the Wetherill process, and refining by re-distillation.

According to H. M. Ridge,[32] in 1913 our consumption of spelter amounted to 224,000 tons, but unfortunately 74% of this amount was imported. The sulphur content of the ore required to produced this amount of spelter would be sufficient to yield 400,000 tons of sulphuric acid of sp. gr. 1·7. The author just mentioned gives in his paper entitled "The Utilisation of the Sulphur Contents of Zinc Ore" a considerable amount of information on the furnaces in use at the present day for roasting zinc blende. The essential condition for all such furnaces, as far as the manufacture of sulphuric acid is concerned, is that they shall be so designed that the gases are rich enough in sulphur dioxide. With an increased zinc-smelting capacity in this country in the near future, there is hope that a large increase will take place in the amount of sulphuric acid made from the sulphur dioxide obtained by roasting blende.

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[30] *J.*, 1917, 803.

[31] *Trans. Amer. Electrochem. Soc.*, 1917, 32, 335; *J.*, 1917, 1238.

[32] *J.*, 1917, 676.

Sulphur recovery by the wet "thiogen" process enables gases to be treated when they contain not less than 5% of sulphur dioxide, and, according to A. E. Wells,[33] it is estimated that the cost of producing sulphur by this means would be about 50*s.* per ton. The process consists of passing the cooled gases through an absorption tower in which the SO_2 is absorbed by the mother liquor resulting from a further stage in the operation and then treating the solution thus obtained with barium sulphide. The reaction results in the formation of a precipitate of barium sulphite and thiosulphate and sulphur from which the free sulphur and one-half of the sulphur existing as thiosulphate can eventually be recovered by distillation. The residual liquor after the precipitate has been removed constitutes the mother liquor used in the absorbing towers.

With reference to the application of the Wetherill process, J. H. and P. M. Gillies[34] propose to utilise the volatilisation method for the recovery of both lead and zinc from complex ores and to smelt the clinker, left on the grate, for a matte. According to their patent, the condensed compounds, consisting chiefly of zinc oxide, lead sulphate, and arsenic and antimony compounds, are to be treated with sulphuric acid, and after purification the zinc sulphate solution is to be electrolysed for the recovery of zinc. The cost should not be prohibitive, provided power can be obtained cheaply, as the electrolysis generates sulphuric acid which can be used as the leaching solution.

It may be mentioned here that J. F. Cregan[35] is of opinion that the Western furnace as used in the Rocky Mountain district in connection with the Wetherill process has greater adaptability than the Eastern type of furnace as employed at Palmerton.

At the present time a large excess of reducing agent is employed in zinc-smelting retorts, chiefly in order to render the charge porous and keep the residue from slagging. W. M. Johnson[36] shows that if ore and coal are finely ground and then briquetted with straw into small pieces or briquettes, good results are obtained with an enormously reduced amount of coal and consequently a lowering of smelting costs.

There has been an increasing tendency to produce high-grade zinc by the re-distillation of commercial spelter, and in this connection the patent of G. C. Fricker[37] is interesting.

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[33] *J. Ind. Eng. Chem.*, 1917, **9**, 872; *J.*, 1917, 1133.

[34] Eng. Pat. 112336; *J.*, 1918, 94A.

[35] *Eng. and Min. J.*, 1917, **104**, 675; *J.*, 1918, 11A.

[36] *Eng. and Min. J.*, 1918, **105**, 370; *J.*, 1918, 270A.

Re-distillation is carried out in a furnace in which the distilling vessel and condensing vessel are in adjacent chambers, the temperature of the latter being so adjusted that it is maintained slightly above the melting-point of zinc. Lead vapour and other impurities are retained by a thick layer of inert porous matter such as coke, which, floating on the surface of the impure metal in the distilling vessel, acts as a filter. The method is sound in principle and has given good results.

G. C. Stone[38] has come to the conclusion that cadmium is practically the sole cause of hardness in commercial spelter.

TIN.

Results of some of the research work carried out by the Tin and Tungsten Research Committee appointed by the Institution of Mining and Metallurgy have now been published in the Transactions of that Institution, and should be consulted by those who are particularly interested in the subject.

The problem of determining the best methods to adopt in order to increase the yield by concentration is evidently being dealt with in a comprehensive manner, for on the one hand results are now available showing the effect of the form of surface in the treatment of slime on Cornish frames, and on the other hand results are given of tests to determine the effect of heating the ore prior to crushing.

There is nothing to report with regard to development in smelting practice.

The high price of tin has resulted in numerous attempts to alter the composition of bearing metals so that less tin might be used and yet as satisfactory results obtained. Although relatively the total amount of tin consumed in the production of solder is much less than for bearing metal, this class of alloy has also received serious attention, and C. W. Hill[39] shows that lead-cadmium and zinc-lead-cadmium alloys can be used as solders with good results. The alloys suggested are the lead-cadmium alloy containing 8–9% of cadmium and the alloy formed by the addition of 5% of zinc to this solder. These solders require a flux, and the best results have been obtained with a flux of the following composition: Sodium chloride 11%, potassium chloride 14%, zinc chloride 65%, ammonium chloride 10%. There are disadvantages connected with the use of these alloys, which no doubt would affect their industrial application, one such disadvantage being the fact that it is necessary to maintain a very even temperature not more than 30° C. above the melting-point of the alloy.

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[37] Eng. Pat. 110970; *J.*, 1917, 1278.

[38] *J. Amer. Inst. Metals*, 1918, **12**, 11; *J.*, 1918, 306A.

[39] *Chem. and Met. Eng.*, 1918, **19**, 170; *J.*, 1918, 588A.

NICKEL.

Practically no developments in the metallurgy of nickel have been reported during the past year; in other words, there is nothing to add to the comprehensive report of the Royal Ontario Nickel Commission. E. P. Mathewson,[40] however, has given the history of the nickel industry since 1910, but this report deals rather with establishment than with metallurgical methods.

ALUMINIUM.

No papers of note dealing with the production of aluminium have appeared during the period under review. Pure aluminium which has been subjected to cold work can be successfully annealed provided time and temperature are properly adjusted. H. C. H. Carpenter and L. Taverner [41] have shown that at a temperature of 550° C. almost complete softening occurs in 1 hour, whereas at 250° C., 600 to 800 hours would be required to produce the same result. This information should be of industrial value, inasmuch as it shows how temperature influences the rate of annealing and also the possibility of using cold-rolled aluminium where the temperature does not exceed 200° C.

Heat treatment can conveniently be carried out on an industrial scale in electric furnaces. The U.S. Aluminium Co. at Massena, N.Y., have been using furnaces of the stationary resistance type for such operations and also for remelting aluminium and making aluminium alloys. The plant, which contains melting furnaces capable of a daily output of 20 tons, is described by D. D. Miller,[42] who shows that the results obtained from the use of electricity as a heating medium were an improved quality of product and a general economy in working.

ALLOYS.

During the past year numerous investigations have been carried out on alloys. In most instances information has been obtained which should be of value to the engineer, but in some cases the investigations have been only of academic interest. The *Journal of the Institute of Metals* should be consulted by those who wish to benefit by the work carried out by metallurgists in this country, and this applies particularly to physico-metallurgical problems.

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[40] *J.*, 1918, 53T.

[41] Inst. of Metals, Sept. 1917; *J.*, 1917, 1098.

[42] *Chem. and Met. Eng.*, 1918, **19**, 251; *J.*, 1918, 626A.

In connection with the preparation and uses of alloys, the application of electric furnaces for the melting of non-ferrous metals and alloys is evidently being extended. T. F. Baily [43] gives details of a furnace of the resistance type used in America for melting bearing bronze and cartridge brass (70/30), and shows that the cost of melting compares favourably with that of furnaces heated by fuel.

The purity of cartridge brass must be maintained if the metal is to conform to specification and pass all the tests, and there is no doubt that electric melting reduces the possibility of introducing impurities. H. W. Brownsdon [44] emphasises the conditions requiring close attention in the manufacture of such brass, viz. (1) the chemical composition of the alloy, (2) the casting of the molten metal, (3) the work to which the alloy is submitted during mechanical operations, and (4) the annealing of the alloy between these operations, and shows that success depends upon the proper control of these conditions. With reference to the first of these conditions, it is stated that fired cartridge cases cannot be used as scrap on account of the antimony introduced from the ingredients of the percussion cap. No doubt researches have been carried out in this connection, and it is to be hoped that a satisfactory method has been evolved.

Platinum substitutes have received special attention. The demand for platinum during the past four years for war purposes has been very heavy, and at the same time there has been a considerable reduction in the world's production. The Russian output has fallen considerably, but this decrease has been partly counterbalanced by the increased output of crude metal mined in Colombia. In 1910 the output of Colombia was 10,000 oz., whereas in 1916 it reached 25,000 oz.[45]

F. A. Fahrenwald [46] states that the alloys in which gold and palladium are the chief constituents give excellent results as platinum substitutes. These alloys, to which the name "rhotanium" has been given, vary considerably in composition and may contain rhodium and silver. The general properties may be summarised as follows: (1) m. pt. below 1450° C., according to composition; (2) sp. gr. 16·0 to 18·5; (3) malleable and ductile and possessing a tensile strength at least equal to platinum; (4) good electrical conductivity; (5) resistant to the action of boiling acids, alkalis, and fused potassium bisulphate equally as well as platinum; and (6) readily welded at a white heat without the aid of a flux. The most serious disadvantages appear to be (1) the difficulties of manufacture on account of the power of palladium to occlude gases and the tendency to segregation of the gold-palladium series, and (2) the necessity of selecting the alloy according to whether it has to withstand the corrosive action of acid or alkali. These alloys are attacked by nitric acid.

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[43] Amer. Electrochem. Soc., 1917; *J.*, 1917, 1276.

[44] *J.*, 1917, 794–796.

[45] *U.S. Commerce Report*, 1917, No. 130; *J.*, 1917, 719.

[46] *J. Ind. Eng. Chem.*, 1917, 9, 590; *J.*, 1917, 882.

Crucibles made of canadium 1 part, palladium 1 part, platinum 2 parts, and nickel 6 parts, have been used for eight months by R. F. Heath[47] in his laboratory, with satisfactory results. Ware of this composition would not withstand either nitric acid or the halogens. The cost is approximately one-half that of platinum.

According to I. L. B. van der Marck,[48] 'Platino' is an alloy of 89 parts gold and 11 parts platinum which is very resistant to caustic potash, but is attacked by sulphuric acid containing nitric acid.

[47] *Met. and Chem. Eng.*, 1917, **17**, 666; *J.*, 1918, 40A.

[48] *Pharm. Weekblad,* 1918, **55**, 149; *J.*, 1918, 244A.

COLOURING MATTERS AND DYES.

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The two outstanding features of the year 1918 as regards the British dye industry are the amalgamation of the two largest dye producers and the Board of Trade scheme of State assistance for the dye industry.

The former of these two developments will in the near future lead to an elimination of unnecessary overlapping in research and manufacture and to more intimate collaboration in dye production between British Dyes, Ltd., and Messrs. Levinstein, Ltd., these two firms having become merged into one organisation, to be called the British Dyestuffs Corporation, Ltd. This merger will place the directorate of the new corporation in control of five factories—namely, the Turnbridge and Dalton works of British Dyes, Ltd., the factory of Messrs. Claus & Co. of Clayton, the older Blackley works of Messrs. Levinstein, and their recently acquired factory at Ellesmere Port. Great extensions are contemplated at the last of these localities, where the site has been secured for a new works to be developed on an even larger scale than the Dalton section of British Dyes.

The two amalgamating firms have to some extent become complementary. During the war period British Dyes have been fully occupied with explosives, intermediates, and certain colours and other materials for Government requirements. Messrs. Levinstein have devoted themselves to colours and synthetic drugs, and more recently to toxic substances for chemical warfare. Moreover, the Manchester firm, which has acquired the synthetic indigo factory, also controls the works of Messrs. Claus, where vat dyes are a speciality.

The new merger has obviously the potentiality of further growth and expansion, so that in the future it may embrace other dye-producing enterprises. The fears of those who on principle distrust trade monopolies on account of their repressive and stagnating tendencies should, however, be allayed by a consideration of the very meritorious and successful efforts in dye production, made during the last four years, by the amalgamating firms and also by other works at present outside the above-mentioned corporation. Certain of these activities are outlined below. Moreover, a further impetus to progress arises from the circumstance that the two branches of the new corporation will remain as separate business entities, although working together under the same directorate.

The Board of Trade scheme of assistance for the dye industry, which might with very considerable national advantage have been initiated in 1915, is intended to help all British firms engaged in dye production. This financial assistance afforded by the Government will take the form of loans and of grants-in-aid for buildings, plant, and research. In return for these privileges the companies thus assisted will be subject to inspection and to a certain degree of Governmental control.[1]

The primary and essential object of this State aid is the firm and permanent establishment of a British industry in dye production yielding a supply of dyes more than sufficient for British requirements, thus leading to a substantial export trade with cost of production brought down to a point which will make competition with the very large scale industry of Germany commercially possible. If, as the result of this policy, the dye industry is established sufficiently to meet British demands at reasonable prices the object of the Government will be attained.

The economic side of the dye question will be the crucial test in the forthcoming years of reconstruction, and on a satisfactory solution of this part of the problem will depend the future of the British industry in fine chemicals in general and of dyes in particular.

The military triumph over the Central Powers won as the result of superhuman feats of heroic fortitude and valour abroad, and of energetic industrial leadership at home, has demonstrated to an astonished world that an extraordinary talent for improvisation is still latent in the English-speaking nations. For the infinitely complex purposes of modern warfare, moribund industries have been restored to vigorous life and new ones created at a cost of capital and labour, which, although extravagantly excessive, has been completely justified, because it has brought us victory and salvation from national disaster and personal enslavement.

The strenuous labours of the last four years have shown that methods for producing colour intermediates can be rapidly improvised when cost is not the primary consideration. Practicable processes for manufacturing the most needful intermediates have been evolved, and certain members of this important group of synthetic products are now being turned out on a very large scale, although at prices which, generally, are very much higher than those which prevailed before the war. A resolute effort at cheaper production is a vital necessity, for without it no feasible mode of protection, whether by tariff or by boycott of foreign goods, will be of any avail. If only this effort is forthcoming it is highly probable that the dye industries of the allied countries will be assisted by the altered social and economic conditions of Germany arising from the military defeat of this highly organised and cleverly camouflaged slave state. These changes may render it less possible for German industrialists to manufacture at very low rates or to "dump" their finished chemical products, and especially dyes, into allied or neutral countries at prices lower than the cost of production. This levelling up of prices by the foreign competitor should meet halfway the process of cheapening which needs to be practised by our manufacturers of fine chemicals.

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[1] *White Paper*, Cd. 9194, 1918.

The economic aspect of our dye industry has recently been emphasised by the Chairman of the Calico Printers' Association, who has also pointed out to what a large extent British dye consumers are still dependent on the Swiss dye producers, especially for the finer specialities essential in calico printing. Certain valuable dyes are either wholly unobtainable, or are still represented by inferior substitutes.

It is, however, becoming recognised more generally that the establishment under peace conditions of a self-contained British dye industry is an arduous task requiring continuous exercise during many years of united efforts in labour, capital, inventive skill, and business organisation of the highest order. To this end there is no royal road or short cut such as was suggested by the alleged "capture" of 257 German dye recipes, to which absurd *canard* regrettable prominence was given by the popular press in the opening weeks of the year.

It is reassuring to turn to the substantial record of progress made by British manufacturers of dyes, who by now are probably under no illusion as to the task which confronts them.

British Dyes, Ltd., have adopted the policy of advertising their principal intermediates and dyewares in the daily press, and among these gazetted products are β-naphthol, p-nitroaniline, benzidine, the dialkylanilines, H-acid, chlorazole blue FFS, and many other colouring matters for the national requirements of the naval and military services.

Messrs. Levinstein, in addition to an increased output of synthetic indigo, have extended considerably their lists of new dyes and intermediates. Among their new acid dyes are durasol acid blue B and SE, corresponding with alizarin saphirol B and SE. The fourteen new vat dyes include carbindol blue R belonging to the hydron blue series. The ranges of direct, chrome, basic, and sulphur dyes have been increased in each series, and the list of intermediate products, drugs, and photographic developers has been lengthened by the inclusion of fifty new items, comprising the principal intermediates for direct cotton colours, together with resorcinol, phthalic anhydride, anthrarufin, isatin, novocain, and several acridine derivatives for use as dyes or antiseptics.

Messrs. L. B. Holliday & Company, who began in 1915 as makers of picric acid by a new process, have embarked on a very active production of dyes and intermediates. The latter section includes anthracene and anthraquinone derivatives as well as intermediates from benzene, toluene, and naphthalene. The colouring matters include tartrazine, azo dyes, sulphur dyes, basic colours, alizarin and anthracene dyes, including the indanthrene group. A special department is devoted to synthetic drugs.

The Solway Dyes Company, having concentrated their efforts exclusively on the production of fast dyes, were led very early in the war period to work out processes for making indanthrene yellow and blue. In the year under review they added to their list of vat dyes by the inclusion of five colouring matters not previously made.

Messrs. Brotherton & Co., who have acquired the Mersey Chemical Works, formerly under German ownership, handle coal-tar products from the crude tar to the finished dyes, and have specialised on metachrome colours, a valuable range of wool dyes giving fast mordanted shades in a single bath.

The British Alizarine Company have extended their output of alizarin red and allied dyes to meet the requirements of the home market and also, in part, the demands of the export trade.

The Clayton Aniline Company, who until April 1918 were devoted to the production of munitions of war, have since resumed their production of aniline, and have also manufactured β-naphthol, *p*-nitroaniline, and dyes of the azo, sulphur, and basic series.

This summary of firms producing dyes and intermediates is by no means complete, and does not include the large gas companies which contribute notably to the supply of intermediates. The survey suffices, however, to indicate that very praiseworthy enterprise is being shown in many directions, and the Board of Trade scheme of assistance should give further impetus and encouragement to these industrial efforts.

Additional help would be given to the synthetic products industries if the Government would regulate the industrial and domestic methods of burning coal. The scientific and economical use of this fuel would lead to an enormous increase in the amount of coal-tar crudes available for the manufacture of dyes and other fine chemicals.

American progress is summarised succinctly in the 'Census of Dyes and Coal Tar Chemicals 1917' issued by the U.S.A. Tariff Commission in 1918. Before the war seven American firms assembled German intermediates and converted them into dyes. During the year under review 190 undertakings were making dyes, drugs and other synthetic products from coal-tar. Of these concerns eighty-one firms manufacture coal-tar dyes from American materials equivalent in total weight to the annual imports before the war, and the total output of the 190 firms was 54,000,000 lb. of a value of about sixty-nine million dollars. More than 1700 chemists and engineers are employed in research and chemical control of this rapidly developing industry, being about 8·8 % of a total personnel of 19,650.

The products now manufactured in the United States include numerous colour intermediates from benzene, toluene, and naphthalene. There still remain to be tackled certain finer dyes derived from anthracene and carbazole. Anthracene was not available in America until the summer of 1917. Carbazole was not manufactured in 1917, but its production was anticipated in 1918.

It is significant of the value attached by Germany to the retention of its monopoly in vat dyes derived from anthracene and carbazole that the cargo carried to America by the submarine *Deutschland* in July 1916 contained 400 tons of dyes chiefly of this class, and in October of the same year another cargo of these dyewares was transmitted by the same agency.

The object of the American Census of dyes is to determine the relation between the home production of dyes and the domestic consumption of these substances. If after five years this production is less than 60% of the consumption of dyes, then the special duties levied under the Revenue Act of September 1916 will no longer be collected. The future protection of the trade in dye and synthetic products is dependent on the growth of the industry within the United States.

In Japan subsidies have been granted by the Government to three companies having a total capital of approximately £800,000, of which about three-fourths is available for dye production. The conduct of the subsidised companies is under strict governmental surveillance.

The terrible jeopardy in which France and Italy have stood in regard to the Teutonic invasions during the greater part of 1918 left the chemists of these menaced countries very little leisure to develop further their projects of dye production. Nevertheless very important constructive work has been carried out in France by the Compagnie Nationale des Matières Colorantes et Produits Chimiques and the Société des Produits Chimiques et Colorantes Français. The former company has established the manufacture of synthetic indigo and alizarin and its derivatives. The latter organisation is dealing with the production on an industrial scale of a wide range of synthetic dyes, including indulines, nigrosines, and azo-colours for wool and cotton. It is significant that the two enterprises have formed a joint "Comité de Direction" with the object of ensuring collaboration and of obviating unnecessary duplication of scientific and industrial efforts.

INTERMEDIATES.

Phenol and its Derivatives.

The production of synthetic phenol is a procedure intended to meet the war requirements for this material, and the early part of 1918 found manufacturers still engaged in devising improvements in the different stages of the process. Continuous sulphonation of benzene with extraction of the product leads to considerable economy of plant and labour. This improvement is based on the fact that benzene extracts between 2 and 3 % of its volume of benzenesulphonic acid from a mixture of this acid with sulphuric acid. Benzene circulates through a series of extractors containing the foregoing mixture, and the sulphonic acid is extracted with water from its solution in the hydrocarbon. Liquid fusion is employed in the next step of the synthesis, a saturated solution of sodium benzenesulphonate being introduced into fused sodium hydroxide at about 300° C.[2]

Economy in strength of sulphuric acid is effected by sulphonating benzene to non-volatile benzenesulphonic acid by excess of sulphuric acid, after which the pressure is reduced and the temperature raised, so that the water formed during sulphonation is removed by distillation. In this way the reaction proceeds completely to the stage of benzenedisulphonic acid.[2a] Benzene when introduced into concentrated sulphuric acid at temperatures above its boiling point is partly sulphonated; the remainder carries off the water formed, and by thus acting as a desiccating agent the continuance of the sulphonation is maintained. The disulphonic acids of chlorobenzene are compounds likely to prove of interest as intermediates. Chlorobenzene-2.4-disulphonic acid is obtained from aniline-2.4-disulphonic acid by the Gattermann diazo-synthesis. Chlorobenzene-3.5-disulphonic acid results from the action of excess of oleum (20% SO_3) on chlorobenzene at 300°. The orientation of the sulphonic groups is noteworthy, and points to isomeric change consequent on the high temperature of reaction.[2b]

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[2] A. G. Peterkin, *Chem. and Met. Eng.*, 1918, **19**, 255; *J.*, 1918, 648A. R. N. Wallach, U.S. Pat. 1274961; *J.*, 1918, 619A.

[2a] C. R. Downs, U.S. Pats. 1279295 and 1279296; *J.*, 1918, 763A.

Oxidation of Aromatic Hydrocarbons.

Aerial oxidation of aromatic hydrocarbons at high temperatures in the presence of catalysts has been practised with very suggestive results. The catalysts are oxides or mixtures of oxides of the metals of the fifth and sixth periodic groups. Toluene and air at 350°–450° over vanadium pentoxide give chiefly benzaldehyde with some benzoic acid. The xylenes similarly treated give methylbenzaldehydes, phthalaldehydes, phthalic acid and its isomerides, the toluic acids, benzoic acid, and benzaldehyde. Naphthalene and air over vanadium pentoxide (450°), or over molybdenum trioxide (500°), give phthalic acid and anhydride, 1.4-naphthaquinone, and benzoic acid. Anthracene yields mainly anthraquinone.[3]

Phthalic Anhydride.

Among the important dyes which remain to be produced economically in England on an industrial scale are the eosins and rhodamines, of which during the war there has been a great shortage in the allied countries. In the case of the eosins the difficulty of production is enhanced by the German monopoly in bromine, a restraint which will soon disappear now that other sources of this valuable element are becoming more available. The other requirements for the manufacture of these xanthone dyes are phthalic anhydride and resorcinol.

The technique of phthalic anhydride production had been perfected in Germany owing to the circumstance that this intermediate was not only used in making certain triphenylmethane dyewares, but was also the starting point in the indigo synthesis of the Badische firm. Naphthalene is employed in this manufacture, being heated with oleum in presence of a catalyst, such as mercuric sulphate. An insufficient amount of acid is first added and the mixture heated to 250°. More acid is subsequently introduced, the heating being then gradually carried to 300° in order to expel the phthalic anhydride.[4]

[2b] Olivier, *Rec. Trav. Chim. Pays-Bas*, 1918, **37**, 307; *J.*, 1918, 762A.

[3] The Seldon Co. and H. D. Gibbs, Eng. Pats. 119517, 119518; *J.*, 1918, 684A.

[4] Greenley, U.S. Pat. 1261022; *J.*, 1918, 406A.

Aromatic Amines.

The reduction of nitrobenzene under varying conditions to yield aniline has been referred to in earlier reports. Electrolytic reduction of this nitro-compound leads to a 43% yield of the important photographic developer, *p*-aminophenol, a substance which also furnishes insoluble colouring matters by oxidation. The experimental conditions must be adhered to closely if a favourable result is to be attained. Platinum electrodes give the most satisfactory reductions, but a carbon cathode may be employed.[5] Electrolytic reduction of *p*-hydroxyazobenzene in alcoholic hydrochloric acid, but not in sulphuric or acetic acid, also furnishes *p*-aminophenol.[5a]

The alkylation of aromatic amines is a problem of perennial interest because of the varying behaviour of bases of this type to the industrially applicable alkylating agents.

Aniline is readily butylated by means of *n*-butyl chloride to furnish either *n*-butylaniline or di-*n*-butylaniline.[6] As is the case with other higher alkyl compounds, the mono-alkyl derivative is the more readily obtainable, the di-*n*-butylaniline being best prepared under pressure. These bases lead to new colour-producing intermediates. The butylation has been extended to *o*- and *p*-toluidine and the nitration products of *n*-butyl-*p*-toluidine have been investigated. It is of interest to note that, contrary to Karrer's statement (*Report*, 1916, p. 93), di-*n*-butylaniline couples normally with diazonium compounds without elimination of a butyl group.

The production of methylaniline by the addition of formaldehyde to aniline in presence of an alkaline reducing agent has furnished the pure base for the purpose of preparing new intermediates.[7] Successive formylation and nitration lead to *p*-nitro-N-methylformanilide, which on reduction with iron and water acidified with formic acid furnishes a new intermediate, *p*-amino-N-methylformanilide.[8]

Acetylation of methylaniline followed by nitration and reduction leads to the next homologue, *p*-amino-N-methylacetanilide. These two intermediates when diazotised yield azo-dyes for wool.[9]

In the report for 1916 the possibilities of employing derivatives of tetrahydronaphthalene were outlined. Further progress has been made in this direction by a detailed study of *ar*-tetrahydro-α-naphthylamine,[10] a base which had formerly been examined from the view point of the formation of azo-dyes about fourteen years ago.[11]

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[5] T. Shōji, *J. Chem. Ind. Tokyo*, 1918, **21**, 117; *J.*, 1918, 459A.

[5a] E. Puxeddu, *Gaz. Chim. Ital.*, 1918, **48**, *II.*, 25; *J.*, 1918, 728A.

[6] Reilly and Hickinbottom, *Chem. Soc. Trans.*, 1917, **111**, 1026; 1918, **113**, 99.

[7] Report 1916.

[8] Levinstein and Morgan, Eng. Pat. 111321, 1916; *J.*, 1918, 5A. Morgan, U.S. Pat. 1273901; *J.*, 1918, 619A.

[9] Morgan and Grist, *Chem. Soc. Trans.*, 1918, **113**, 688; *J.*, 1918, 573A.

The production of monomethylaniline is rendered difficult because of the tendency for direct methylating agents to carry the process to the tertiary or even to the quaternary stage.

Vapours of aniline and methyl alcohol passed over alumina heated at 400°–430° give rise to a mixture of methyl- and dimethyl-aniline. Methylaniline by further interaction with methyl alcohol gives dimethylaniline, and similar methylations can be effected with the toluidines.[12]

The sulphonation of aromatic amines is not only of scientific interest, but of great industrial importance. This process applied to β-naphthylamine leads entirely to heteronuclear substitution, the sulphonic group entering the unsubstituted ring. At temperatures ranging from 20° to 80°, 97 to 99·5% of the sulphonation product consists of a mixture of β-naphthylamine-5-sulphonic and β-naphthylamine-8-sulphonic acids. Only at higher temperatures are these acids converted into the 2.6 and 2.7 acids.

The memoir under review contains the results of quantitative experiments on isomeric change showing the effect of temperature, strength of acid, and duration of reaction on the migration of the sulphonic group. These observations are of importance in connexion with the production of colour-producing intermediates from β-naphthylamine.[13]

The foregoing and other sulphonations can be modified by the employment of chlorosulphonic acid, of which large quantities are now available. Anthranilic acid, treated with this sulphonating agent in an inert solvent or in presence of concentrated sulphuric acid, yields 4-sulpho-1-aminobenzene-2-carboxylic acid,[14] an intermediate used in preparing dyes of the diamond black type.

Diamines of the benzidine series do not usually give rise to substantive cotton dyes when substituted with univalent groups in the meta-position with respect to the amino-radicals. When, however, the meta-substituent is a bivalent group—such as the sulphone radical, attached to both aromatic rings—then the resulting complex gives rise to direct cotton dyes.[14a]

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[10] Green and Rowe, *Chem. Soc. Trans.*, 1918, **113**, 955.

[11] Morgan, Micklethwait, and Winfield, *loc. cit.*, 1904, **85**, 7 and 36; Morgan and Richards, *J.*, 1905, **24**, 652.

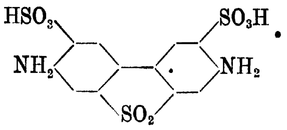
[12] Mailhe and de Godon, *Compt. rend.*, 1918, **166**, 467; *J.*, 1918, 234A.

[13] Green and Vakil, *Chem. Soc. Trans.*, 1918, **113**, 35; *J.*, 1918, 118A.

[14] Farbenfabr. vorm. F. Bayer, Ger. Pat. 307284; *J.*, 1918, 619A.

[14a] Ryan, Algar, and O'Connell, *Proc. Roy. Irish Acad.*, 1918, **34** (B), 85. Ryan and Glover, *loc. cit.*, 97; *J.*, 1918, 762 and 763A.

Benzidine-2.2′-sulphone-5.5′-disulphonic acid



has been examined from this standpoint and its diazo-derivatives have been prepared with the representative phenols, naphthols, and aminonaphthols and their sulphonic acids. Cotton colours giving a wide range of shades were thus obtained.

The Goldberg synthesis of substituted diphenylamine derivatives is a condensation process having a wide application. Aniline or a homologous aromatic primary amine is heated with the halogenated derivative of an aromatic nitro compound in nitrobenzene solution in the presence of dry potassium carbonate and cuprous iodide. Aniline and *p*-nitrochlorobenzene when condensed in this way yield *p*-nitrodiphenylamine. A detailed study of this condensation has recently been made, leading to numerous nitrated diphenylamine compounds.[14a]

DI- AND TRI-PHENYLMETHANE DYES.

The past year's contributions to the chemistry of the basic dyes of this series are chiefly of theoretical interest.

In the Heumann synthesis for crystal violet or its analogues, carbon tetrachloride and a tertiary aromatic amine are condensed with aluminium chloride; in the case of dimethylaniline the resulting dye is crystal violet. It is now suggested that the initial product of this condensation is the ketochloride, $CCl_2[C_6H_4 \cdot N(CH_3)_2]_2$, inasmuch as a small amount of tetramethyldiaminobenzophenone is obtained by adding the condensation product to ice-cold water. Further evidence is obtained by using acetanilide instead of dimethylaniline, when a very favourable yield of diaminobenzophenone is furnished after hydrolysing the product obtained by adding the condensation product to water. Other anilides give equally good results.[15]

Werner's co-ordination theory[16] of inorganic structure has been applied to quinonoid dyes, magenta being represented by the formula:

$$[(NH_2 \cdot C_6H_4)_3C]Cl.$$

It has also been suggested that in strongly acid solutions of the triphenylmethane bases these substances form salts in which acid residues are attached to the methane carbon atom either by the exercise of a fifth or sixth valency of this atom or by its residual affinity.[17] This view must, however, in our present state of knowledge be regarded as highly speculative. The behaviour of carbon in its many and diverse combinations is consistent with the hypothesis that its valency, although occasionally less, is never greater than four and that its maximum co-ordination number is also four.

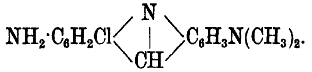
[14a] Ryan, Algar, and O'Connell, *Proc. Roy. Irish Acad.*, 1918, **34** (B), 85. Ryan and Glover, *loc cit.*, 97; *J.*, 1918, 762 and 763A.

[15] Fierz and Koechlin, *Helv. Chim. Acta*, 1918, 1, 210; *J.*, 1918, 685A.

[16] *loc. cit.*

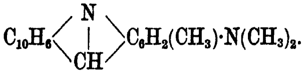
Acridine compounds now possess a dual interest, since they find employment either as dyes or as drugs.

New orange-yellow dyes for leather have been prepared recently. Formylchloro-*m*-phenylenediamine is condensed with *m*-amino-dimethylaniline hydrochloride; the resulting acridine has the formula:



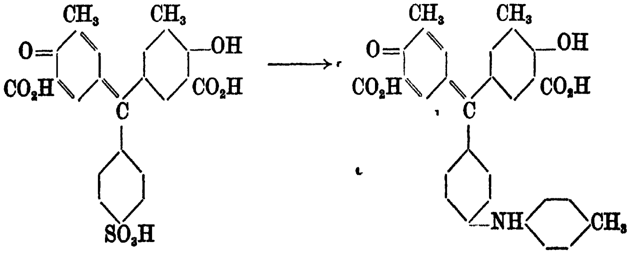
$$NH_2\cdot C_6H_2Cl\left\langle\begin{matrix}N\\ |\\ CH\end{matrix}\right\rangle C_6H_3N(CH_3)_2.$$

Formyl-β-naphthylamine condensed with *m*-diamines of the benzene series gives rise to another group of new acridines, of which the following formula represents a typical example:[18]



$$C_{10}H_6\left\langle\begin{matrix}N\\ |\\ CH\end{matrix}\right\rangle C_6H_2(CH_3)\cdot N(CH_3)_2.$$

The acidic triphenylmethane dyes from *o*-cresotic acid are still being investigated. Benzaldehyde is condensed with this acid (2 mols.);



I. II.

oxidation of the leuco-derivative gives the quinonoid compound, which is sulphonated to the sulphonic acid (I) and this on heating with *p*-toluidine gives the toluidino-derivative (II). This product on sulphonation yields the dye (III),

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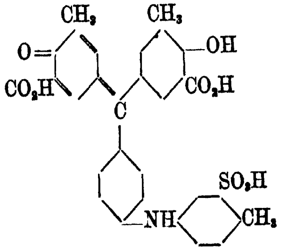
[17] Kehrmann, *Ber.*, 1918, 57, 468; *J.*, 1918, 364A.

[18] Grünhagen, U.S. Pat. 1255740; *J.*, 1918, 236A.



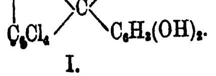
III.

which when printed on cotton with a chrome mordant gives bright violet shades.[19]

Xanthone Dyes.

Emphasis has already been given in the earlier part of this report to the importance of producing economically the important eosins and rhodamines. The starting-point in this manufacture is the condensation of phthalic anhydride with either resorcinol or a dialkylamino-*m*-phenol. Various condensations with phthalic anhydride and its halogenated derivatives are being investigated in America, and the experience gained in these researches cannot fail to advance the technique of the production of xanthone dyes.

Resorcinol and tetrachlorophthalic acid heated at temperatures not exceeding 131° yield an intermediate, *o*-2′.4′-dihydroxybenzoyltetrachlorobenzoic acid to which the following constitution (I) is ascribed:



I.

This compound at 227° decomposes into tetrachlorofluorescein and tetrachlorophthalic anhydride.[20]

The results of a comprehensive series of researches on the constitution and colour of phthalic acid derivatives have been published. In the course of this work phthalic and the three dichlorophthalic acids have been iodinated and tetraiodofluorescein and octoiodofluorescein (tetraiodoerythrosin) have been prepared.[21]

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[19] Weiler, U.S. Pat. 1244149; *J.*, 1918, 5A.

[20] Orndorff and Adamson, *J. Amer. Chem. Soc.*, 1918, 40, 1235; *J.*, 1918, 620A.

Various derivatives and homologues of phenolphthalein have been examined, including phenoltetraiodophthalein[22] and α-naphtholphthalein.[23]

AZO-DYES.

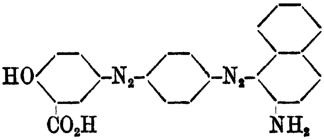
The researches in this large class of dyes still centre largely on the production of new dyes capable of forming fast lakes with chromium or copper salts.

In the case of the former metal very favourable results are produced by the single bath method known as metachroming, in which the dye and mordant are affixed to the fibre concurrently, forming the chrome lake. The metachrome mordant is a mixture of sodium or potassium chromate and ammonium sulphate or a bichromate rendered alkaline with ammonia.

A simple dye of this series isomeric with metachrome brown Y is produced by coupling diazotised picramic acid either with pure *p*-cresol or with mixtures of cresols containing this isomeride; the chrome lake on wool is olive-brown and fast to light.[24]

In some instances level shades can be produced by this method of dyeing even when the dyes are almost insoluble in the dye-bath.

The disazo-dye,



produced by coupling diazotised *p*-aminobenzeneazosalicylic acid with β-naphthylamine, is insoluble in water, but when used as a gelatinous mass it forms a colloidal solution dyeing wool with metachrome mordant in bright red shades; it also dyes unmordanted cotton in pink to red shades.[25]

The mordant may also be employed in a colloidal condition, as for example one of the hydrated forms of chromic oxide preferably in a freshly precipitated condition. Alternatively a normal chromate may be employed with or without the addition of a reducing agent or an alkali-fixing agent or both of these materials.[26]

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[21] Pratt, Coleman and Perkins, *J. Amer. Chem. Soc.*, 1918, **40**, 198, 236; *J.*, 1918, 119A.

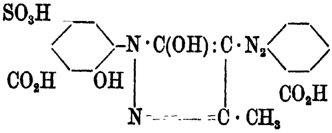
[22] Pratt and Shupp, *J. Amer. Chem. Soc.*, 1918, **40**, 254; *J.*, 1918, 120A.

[23] Werner, *Chem. Soc. Trans.*, 1918, **113**, 20; *J.*, 1918, 119A.

[24] Eng. Pat. 113181; *J.*, 1918, 202A.

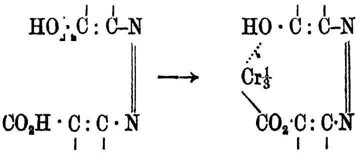
[25] E. F. and H. W. Ehrhardt, Eng. Pat. 113195; *J.*, 1918, 202A.

Mixed azo-dyes containing pyrazolone residues are amenable to chroming if they contain a suitable arrangement of hydroxyl groups. For example, the azo-compound (I) resulting from the coupling of diazotised anthranilic acid with 5′-sulpho-3′-carboxy-2′-hydroxy-1-phenyl-3-methyl-5-pyrazolone dyes wool from an acid bath in yellow shades becoming brownish yellow on after-chroming.[27]



I.

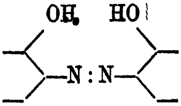
When reacting in its enolic form this dye contains the lake-forming complex (II) leading to the co-ordination ring (III).



II. III.

The singular properties of co-ordinated copper compounds have been utilised in the production of azo-dyes for wool.

Hydroxyazo-dyes containing the following complex



IV.

are very sensitive to copper and cannot be dyed from vessels of this metal because of the staining which occurs. When, however, the azo-dye is first combined with copper, a soluble co-ordinated copper derivative is produced,

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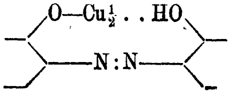
[26] Soc. Chem. Ind. Basle, Eng. Pat. 116535; *J.*, 1918, 460A.

[27] Soc. Chem. Ind. Basle, U.S. Pat. 1270325; *J.*, 1918, 573A.



V.

in which the metal is not detected by such analytical reagents as caustic soda, sodium carbonate, or ammonia. These copper derivatives can be used as dyes, when they show considerable fastness to washing and to light, and moreover they are no longer affected by copper. *o*-Aminophenol and the *o*-aminonaphthols and their sulphonic and carboxylic derivatives can be used as the diazotisable compounds, and these may be coupled with all such phenols as give *o*-hydroxyazo-dyes. Phenylmethylpyrazolone and its derivatives, β-diketones, and β-ketocarboxylic esters may also be employed as coupling agents. These substances furnish the second hydroxyl-group of the foregoing complexes by reacting in their enolic forms (*cf.* formulæ II and III). 3-Oxy-1-thionaphthene can be used for a similar reason, and the employment of *m*-phenylenediamine and its homologues makes it evident that the foregoing co-ordination can occur between copper and an adjacent amino-group.[28]

These copper derivatives are produced either by combining the azo-dyes with copper salts or by performing the azo-coupling in the presence of copper compounds.

The copper is replaceable by chromium from chromium fluoride, when "half chrome" compounds are produced which can be dyed as such and afterwards fully chromed. The copper co-ordination compounds are also susceptible to chroming. The reaction has been extended to the production of nickel, iron, cobalt, aluminium, vanadium, and uranium compounds of the hydroxyazo-dyes.[29]

Isatin and resorcinol condense in alkaline media to yield an alkali-soluble product which couples with diazo-oxides to form hydroxyazo-dyes amenable to chroming.[30]

In certain cases where the coupling of an *ortho*diazo-oxide occurs with difficulty, the reaction is facilitated by effecting the change in the presence of copper compounds. Naphthalene-1-diazo-2-oxide-4-sulphonic acid gives a poor yield of azo-compound with α-naphthol-5-

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[28] Eng. Pats. 1611, 12219 and 16916, 1915; *J.*, 1916, 301; 1917, 78.

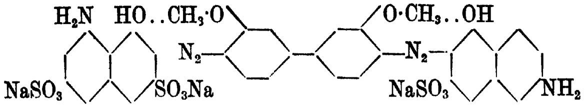
[29] Eng. Pats. 13204, 15127, 15456, 16803, and 16916 of 1915; *J.*, 1916, 419, 1104, 1255; 1917, 78.

[30] Ger. Pat. 290599 and 304674; *J.*, 1916, 530; 1918, 460A.

sulphonic acid, but when copper sulphate is added to the alkaline solution of the latter at 0°–40°, a quantitative yield of the copper compound of the azo-dye is obtained.[31]

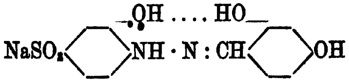
An interesting series of copper compounds of substantive dyes is produced by treating with copper or a copper compound the bisazo-dye obtained from a substituted paradiamine containing at least one ortho-alkyloxy-group with respect to an amino-group and either two molecules of J-acid (2-amino-5-naphthol-7-sulphonic acid) or one of its N-substituted alkyl, aryl, or acyl derivatives, or one molecule of J-acid or its derivatives and one molecule of a 1.8-aminonaphtholsulphonic acid.

The following dye may be formulated as an example of this group:



The copper compound is soluble and dyes directly on cotton and also on wool, silk, mixed fabrics, leather, or straw. These copper derivatives are noteworthy as showing co-ordination properties (*e.g.*, fastness to alkalis), although one of the reacting groups is an alkyloxy radical and not hydroxyl as is usually the case.[32]

A significant extension of the application[33] of co-ordinated copper compounds in dyeing to the hydrazone colours has recently been described. In the production of these complex hydrazones a hydroxyacylhydrazine or an acylhydrazinecarboxylic acid is condensed with an aldehyde or ketone of the benzene, naphthalene, or furfurol series. For instance, the sodium salt of the hydrazone from 1-hydroxy-2-phenylhydrazine-4-sulphonic acid and resorcylaldehyde is treated with copper sulphate, and the resulting copper derivative of the dye (I) is precipitated with salt as a greenish yellow compound dyeing wool in yellowish green shades from an acid bath.



I.

It is evident that co-ordination relationships can exist between the copper radical and the hydroxyl groups contiguous to the hydrazone complex as shown in the foregoing formula.

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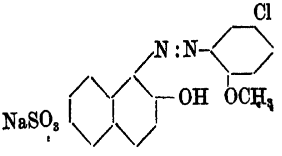
[31] **Soc. Chem. Ind. Basle, Eng. Pat. 116530; *J.*, 1918, 459A.**

[32] **Soc. Chem. Ind. Basle, Eng. Pat. 113141; *J.*, 1918, 202A.**

[33] **Soc. Chem. Ind. Basle, Eng. Pat. 114189; *J.*, 1918, 235A.**

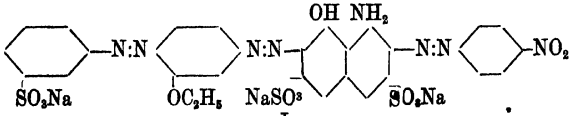
Additions are still being made to azo-dyes for wool. 4-Chloro-*o*-anisidine when diazotised and coupled with α- or β-naphtholsulphonic acids gives bright red dyes fast to milling or fulling. The compound with Schäfer acid may be formulated as representative of the group.[34]



To the foregoing employment of a chlorinated intermediate may be added the preparation of tetrachlorotartrazine produced by condensing dihydroxytartaric acid with 2 molecular proportions of 2.5-dichlorophenylhydrazine-4-sulphonic acid. The dye gives intense yellow shades on wool and silk.[35]

The two chlorinated intermediates employed in the foregoing examples indicate the growing importance of the industrial chlorination of benzene, since the starting material for their production is in both instances 1.4-dichlorobenzene.

The study of the azo-dyes from *m*-phenetidine has been continued. The most promising colour of the series is produced by coupling this base with diazotised metanilic acid, rediazotising the resulting amino-azo-derivative, and coupling further with *p*-nitrobenzeneazo-8-amino-α-naphthol-3.6-disulphonic acid (from *p*-nitroaniline and H-acid). The trisazo-dye (I) gives bluish green to black shades of wool, fast to potting and fulling.[36]



I

The Diazo-Reaction.

Further study of the *p*-diazoimides has led to the production of comparatively stable compounds of this series, containing acetyl groups and derived from the acetyl derivatives of nitro-*p*-phenylenediamine and 2.6-dichloro-*p*-phenylenediamine. As examples of this series the two isomeric nitro-compounds may be formulated :

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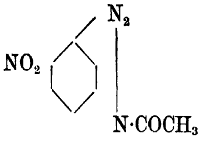
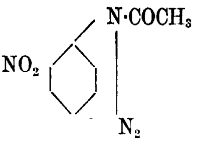
[34] British Dyes, Ltd., J. Turner, and H. Dean, Eng. Pat. 113825; *J.*, 1918, 235A.

[35] L. B. Holliday and A. Clayton, Eng. Pat. 113510; *J.*, 1918, 203A.

[36] Reverdin, Rilliet, and Vernet, *Arch. Sci. Phys. Nat.*, 1918, 46, 74; *J.*, 1918, 541A.





These acetylated *p*-diazoimides couple additively with the phenols and their sulphonic acids and with the more active aromatic amines, giving rise to two parallel series of isomeric azo-derivatives.[37]

A point which is not without importance in the manufacture of hydroxyazo-dyes has been elucidated during the past year. It is known that in certain cases the coupling of naphtholsulphonic acids with diazonium salts is retarded or inhibited by the steric hindrance of substituents in the naphthalene nucleus. The couplings with β-naphthol-8-sulphonic acid or with β-naphthol-6.8-disulphonic acid give examples of this retardation, the result of which is that the crude azo-dyes contain diazo-oxides, compounds of the type $HSO_3{\cdot}C_{10}H_6{\cdot}O{\cdot}N_2R$, in which the diazo-group has not entered into the ring but has remained attached to the phenolic oxygen. These diazo-oxides are decomposed on heating, giving rise to tarry products.

It is extremely likely that this preliminary attachment of the diazo-group to phenolic oxygen is the first stage in the formation of any hydroxyazo-compound produced by direct coupling, but with the more reactive phenols and their derivatives isomeric change occurs so rapidly that the first product has only a very fleeting existence. In the case of *p*-nitrophenol and *p*-bromobenzenediazonium chloride the primary product has been isolated. Auwers has raised the question as to whether such compounds are ethers, $R{\cdot}O{\cdot}N : N{\cdot}R'$, or diazonium salts, $R{\cdot}O{\cdot}NR' : N$. To this query Dimroth[38] has now furnished a reply. Taking advantage of the great stability of the following diazonium salts, 4-benzoylaminonaphthalene-1-diazonium chloride, and 4-acetylaminobenzene-1-diazonium chloride, first discovered by Morgan and Wootton in 1907,[39] he has coupled these with phenolic substances ranging in acidic strength from picric acid to pentamethylphenol. The molecular conductivities of the products have been determined in 80% acetone. The results show that the compound with strongly acidic phenols, picric acid and 2.4-dinitrophenol, are true diazonium salts with the same electrical conductivities as the original chlorides or the corresponding trichloroacetates. The weaker phenols and certain enolic compounds give true ethers with conductivities as low as that of *p*-nitrobenzeneazomethyl ether, $NO_2{\cdot}C_6H_4{\cdot}N : N{\cdot}OCH_3$. Hence the chemical nature of the diazo-oxide depends on the acidic strength of the coupling phenol.

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[37] Morgan and Cleage, *Chem. Soc. Trans.*, 1918, **113**, 588.

[38] Dimroth, Leichtlin, and Friedemann, *Ber.*, 1917, **50**, 1534; *J.*, 1918, 118A.

[39] *Chem. Soc. Trans.*, 1907, **91**, 1311.

VAT DYES.

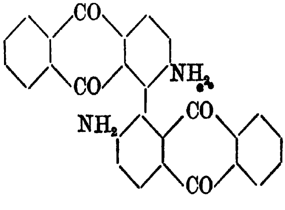
Research in this group of colouring matters has in the past year been directed chiefly towards the anthraquinone section. These investigations include improvements in the production of intermediates and in the purification of the dyes themselves.

Indanthrene Series.

Sodium anthraquinone-β-sulphonate, the starting material for indanthrene, is salted out by sodium sulphate from a mixture of mono- and di-sulphonated derivatives of anthraquinone.[40] The next step, leading to β-aminoanthraquinone, is facilitated by heating anthraquinone-β-sulphonic acid with ammonia in presence of an aromatic nitro compound; the ammonium sulphite eliminated reduces the nitro compound to the corresponding amine.[41]

Crude indanthrene blue (N-dihydro-1.2.2′.1′-anthraquinoneazine) is freed from the yellow colouring matter present as an impurity by boiling the 10% paste with aqueous sodium hypochlorite (sp. gr. 1·15). After cooling, the excess of oxidising agent is removed by washing. The soluble salts of other oxidising acids such as chloric, permanganic, and persulphuric acids may be employed in this purification.[42]

In various syntheses of flavanthrene (indanthrene yellow) it has been assumed that the intermediate product is 2.2′-diamino-1.1′-dianthraquinonyl.



This substance has now been isolated in the form of red needles changing into flavanthrene at 250°.[43]

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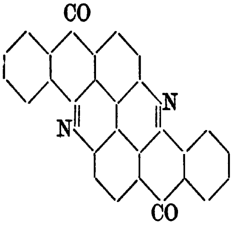
[40] The Barrett Co., U.S. Pat. 1260535; *J.*, 1918, 296A.

[41] Dutoit, U.S. Pat. 1255719; *J.*, 1918, 202A.

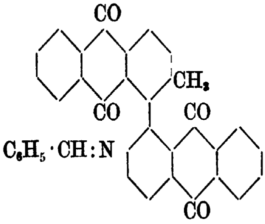
[42] British Dyes, Ltd., Turner and Segaller, Eng. Pat. 113489; *J.*, 1918, 202A.

[43] Scholl and Dischendorfer, *Ber.*, 1918, 57, 452; *J.*, 1918, 364A.

Pyranthridone (I), a vat dye subliming in brownish-yellow needles, giving a violet blue hydrosulphite vat and dyeing cotton in orange red shades after prolonged exposure, has now been synthesised from 1-chloro-2-methylanthraquinone and 2-benzylidene-amino-1-chloroanthraquinone in the presence of copper powder. The intermediate compound is 2-methyl-2′-benzylidene-amino-1.1′-dianthraquinonyl (II).[44]

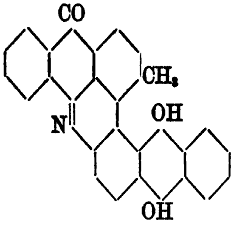


I.

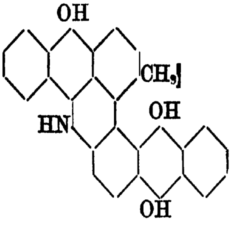


II.

Pyranthridone gives with cold hydrosulphite a magenta-red vat containing a dihydro-compound (III). On warming the vat becomes violet blue and then contains the tetrahydro-compound (IV).



III. Red vat.



IV. Blue vat.

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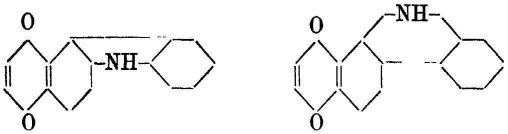
[44] Scholl and Dischendorfer, *Ber.*, 1918, 51, 441; *J.*, 1918, 364A; *cf.* Ger. Pat. 307399.

On reduction with hydriodic acid and phosphorus at 210° pyranthridone yields dihydropyranthridine, $C_{29}H_{19}N$, which, sublimed over heated copper, yields pyranthridine, $C_{29}H_{17}N$.

Complex vat dyes giving yellow vats and dyeing in violet black shades are produced on condensing the carbazole-naphthaquinones with a substance containing a reactive hydrogen capable of condensation with benzo- or naphthaquinones. Tolucarbazole-naphthaquinone condensed with oxythionaphthene gives a dye having the above vat properties.[45]

The carbazole-naphthaquinones have the following constitutions:

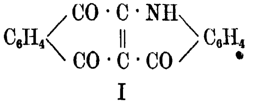


and are produced by oxidising the corresponding hydroxynaphthalenecarbazoles. These complex quinones react with amines, sulphinic acids, indoxyl, or oxythionaphthene, and the condensation products furnish vat dyeings on reduction.

Among the polynuclear hydrocarbons and cyclic bases the prevailing tendency is for a succession of rings to double on themselves, and on this account it is difficult to synthesise compounds built up of more than five rings arranged so that the centres of these rings are in the same straight line (linear compounds).

Two such linear compounds have been synthesised containing respectively four and five rings.

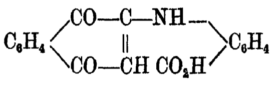
Phenonaphthacridonequinone (I)



$$C_6H_4\left\langle\begin{array}{c}CO\cdot C\cdot NH\\ \| \\ CO\cdot C\cdot CO\end{array}\right\rangle C_6H_4$$

I

is obtained by condensing α-naphthaquinone with anthranilic acid to anilino-α-naphthaquinonecarboxylic acid (II).



$$C_6H_4\left\langle\begin{array}{l}CO—C—NH— \\ \quad\quad \| \\ CO—CH\ CO_2H\end{array}\right\rangle C_6H_4$$

II.

This intermediate condensed with concentrated sulphuric acid at 150° yields phenonaphthacridonequinone. This quinone forms a blue alkaline hydrosulphite vat from which cotton is dyed in orange yellow shades. Quinacridonequinone (III), a yellow powder,

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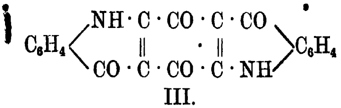
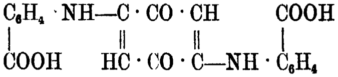
[45] Schmidt and Kalle & Co., U.S. Pat. 1261858; *J.*, 1918, 365A.



$$C_6H_4\left\langle\begin{array}{ccccc} NH\cdot & C & \cdot CO\cdot & C & \cdot CO\\ & \| & & \| & \\ CO\cdot & C & \cdot CO\cdot & C & \cdot NH\end{array}\right\rangle C_6H_4$$

III.

is produced by dehydrating *p*-benzoquinone-dianthranilic acid (IV)



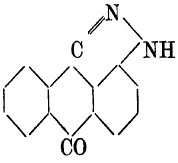
$$\begin{array}{ccccccc} C_6H_4 & \cdot NH- & C & \cdot CO\cdot & CH & & COOH\\ | & & \| & & \| & & |\\ COOH & & HC & \cdot CO\cdot & C & -NH\cdot & C_6H_4\end{array}$$

IV.

with concentrated sulphuric acid at 145–155°.

On reduction this five-ringed linear compound yields a bluish-violet powder which, however, is insoluble and hence not applicable to the vat process.[46]

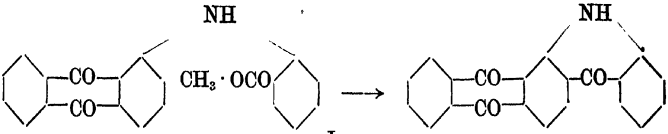
A vat dye giving fast golden yellow shades from a bluish green vat is produced by warming the benzyl derivative of pyrazole-anthrone yellow with concentrated sulphuric acid. This yellow is itself produced by fusing pyrazole-anthrone (I) with caustic alkali. The condensation product can be mono- and di-alkylated.[47]



I.

1-Aminoanthraquinone can be made the starting point of a series of vat dyes by condensation with substituted methyl *o*-chlorobenzoic esters.

The parent substance of the series, 1.2-phthaloylacridone ("anthraquinone-2.1-acridone," I) is prepared by condensing 1-aminoanthraquinone with methyl *o*-chlorobenzoate ; the following are the stages in the process :



I.

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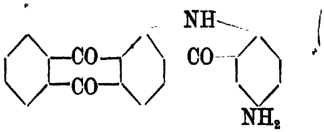
[46] W. St. Leśnianski, *Ber.*, 1918, 57, 695 ; *J.*, 1918, 540A.

[47] Chem. Fabr. Griesheim-Elektron, Ger. Pat. 302260 ; *J.*, 1918, 365A. Eng. Pat. 14103, 1915 ; *J.*, 1916, 1104.

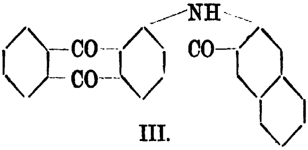
This acridone dyes from a hydrosulphite vat in reddish-violet shades. The amino-compound, 6-amino-1.2-phthaloylacridone (II),



II.

dyes from the vat in bluish violet shades.

1.2-Phthaloyl-6.7-benzoacridone (III)

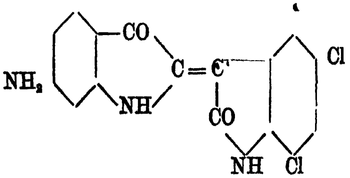


III.

forms dark violet needles and dyes from a green vat in bluish violet shades, thus differing from its isomeride, 1.2-phthaloyl-5.6-benzoacridone (indanthrene red BN extra), which gives red shades.[48] The intermediate compound required in the preparation of this vat dye is anthraquinonyl-2-amino-3-naphthoic acid obtained from 1-chloroanthraquinone and 2-amino-3-naphthoic acid or in the form of its ester from 1-amino-anthraquinone and methyl 2-chloro-3-naphthoate. This acid condensed with warm alkaline hydrosulphite yields the vat from which the acridone separates on aerial oxidation.

Indigoid Dyes.

Vat dyes of the indigoid series are produced by condensing substituted indoxyls with halogen derivatives of isatin. The product from 6-aminoindoxyl and 5.7-dichloroisatin is a dark brown crystalline powder,



dyeing cotton from the vat in yellowish brown shades fast to light, washing, and chlorine.[49]

Isatin is becoming increasingly important as an intermediate in the production of vat dyes of the indigoid series. α-Isatin anilide condenses with sulphazone to form an indigoid vat dye. Sulphazone also furnishes a similar dye when condensed with thionaphthene-quinone-anilide. These two dyes, which have no great affinity for the fibre, do not contain the accepted indigo chromophor CO·C = C·CO, but they possess the modified chromophor formulated by Claasz (*J.*, 1916, 1150).

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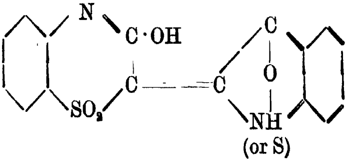
[48] Ullmann and Dootson, *Ber.*, 1918, 51, 9; *J.*, 1918, 178A. *Cf.* Ger. Pat. 237236; *J.*, 1911, 1153.

[49] Bauer and Herre, U.S. Pat. 1266092; *J.*, 1918, 541A.



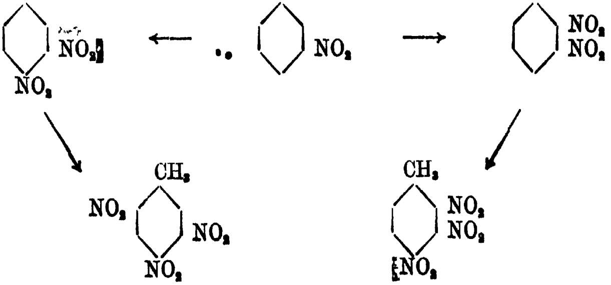
Sulphazone condensed with β-isatinanilide yields a substance devoid of tinctorial products; the relation of this product to the above NH-compound is that of indirubin to indigotin.[50]

SULPHIDE DYES.

The hydrocarbons benzene and toluene, which are the two crudes furnishing a large proportion of the sulphide dyes and their intermediates, have been so greatly in demand for the manufacture of high explosives that diligent search has been made during the war period for substitutes which would produce similar results by interaction with polysulphides.

Naturally occurring waste products—such as rice hulls, and tobacco-stems—have been employed in the sulphide fusion.[51]

The nitration of toluene leads to the formation of a small proportion of *m*-nitrotoluene, which becomes further nitrated to di- and tri-nitrotoluenes having sensitive nitro-groups readily removed by aqueous caustic alkalis.



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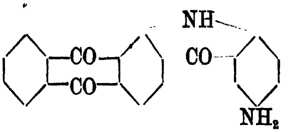
[50] Herzog, *Ber.*, 1918, 51, 516; *J.*, 1918, 407A.

[51] Suzuki, U.S. Pats. 1244795 and 1244796; *J.*, 1918, 5A.

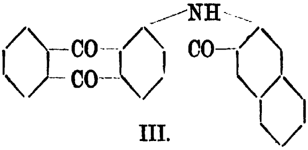
This acridone dyes from a hydrosulphite vat in reddish-violet shades. The amino-compound, 6-amino-1.2-phthaloylacridone (II),



II.

dyes from the vat in bluish violet shades.

1.2-Phthaloyl-6.7-benzoacridone (III)



III.

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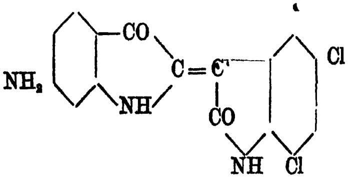

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[48] Ullmann and Dootson, *Ber.*, 1918, **51**, 9; *J.*, 1918, 178A. *Cf.* Ger. Pat. 237236; *J.*, 1911, 1153.

[49] Bauer and Herre, U.S. Pat. 1266092; *J.*, 1918, 541A.

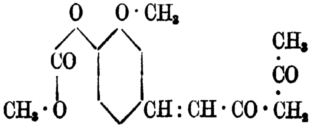
Logwood dyers have found favourable opportunities of utilising their practical acquaintance with this highly skilled branch of the dyeing trade.

Records have been published during the past year of researches on the red words. Camwood contains an insoluble colouring matter isosantalin, $C_{23}H_{18}O_6(OCH_3)_2$, isomeric with the santalin of sanderswood. These insoluble compounds are accompanied respectively in the dyewood by the more soluble deoxyisosantalin and deoxysantalin, $C_{22}H_{16}O_3(OCH_3)_2$ or $C_{22}H_{18}O_5(OCH_3)_2$. Santalin is also obtainable from barwood, which also contains santal, $C_{15}H_9O_5(OCH_3)_3$, and santalone, $C_{22}H_{15}O_4(OCH_3)_3$.[58]

A South African species of *Hœmatoxylon* was found to resemble Brazil wood rather than logwood in its dyeing properties.[59]

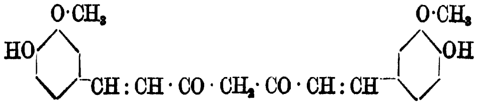
The dyes from *Sorghum technicum* (orange shades on silk) and from *coprosma*, a genus related to the madder plant, have been examined tinctorially.[60]

A synthesis of curcumin has been effected during the past year from α-carbomethoxyferuloyl chloride, this reagent being prepared by successively condensing ferulic acid with methyl chlorocarbonate and by treating the resulting carbomethoxyferulic acid with phosphorus pentachloride.[61] Condensation with ethyl sodioacetoacetate leads to a condensation product which on hydrolysis loses water and ethyl alcohol yielding methoxyferuloylacetone,



I.

This product on account of its active methylene group reacts with a second molecule of carbomethoxyferuloyl chloride leading to an acetyl derivative of dicarbomethoxydiferuloylmethane. Successive hydrolyses remove the acetyl and carbomethoxyl groups giving rise to diferuloylmethane (II.) which is identical in all respects with curcumin.



II.

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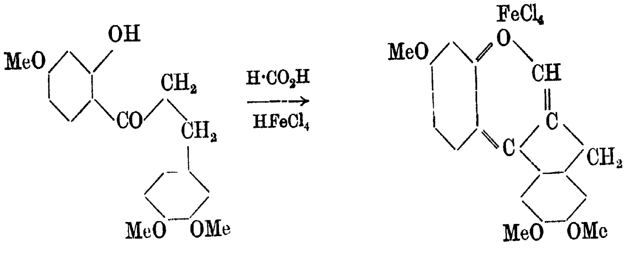
[58] P. O'Neill and A. G. Perkin, *Chem. Soc. Trans.*, 1918, **113**, 125; *J.*, 1918, 235A.

[59] A. G. Perkin, *J. Soc. Dyers and Col.*, 1918, **34**, 99; *J.*, 1918, 296A.

[60] *J.*, 1918, 332A and 407A. [61] Fischer and Hoesch, *Annalen*, 1912, **391**, 358.

The mono- and di-hydroxydicinnamoylmethanes having the same open chain as in II. have been found to resemble curcumin [62] in being substantive dyes for cotton.

The constitutions of brazilin and haematoxylin and their oxidation products, brazilein and haematein, were determined by Perkin and Robinson ten years ago,[63] and evidence in confirmation of these views is still being collected. Brazilein is transformed by mineral acids into orange-red compounds—the so-called *iso*brazilein salts. These products have now been synthesised. Veratrylidene pæanol, obtained by condensing pæanol and veratraldehyde is reduced to dihydrobutein trimethyl ether (I.); the latter on prolonged boiling with zinc chloride and formic acid, and subsequent treatment with hydrochloric acid and ferric chloride, yields *iso*brazilein ferric chloride trimethyl ether (II.).



I. II.

From this compound simpler pyrrylium oxonium salts ar obtainable.[64]

DYES FROM WASTE PRODUCTS.

The waste liquors of the sulphite cellulose industry contain lignin sulphonates and lignone-sulphonates. These substances are separate by salting out, when the former is precipitated, while the latter remai in solution and is converted into azo-dyes by coupling with diazotis aniline, 4-nitro-2-toluidine, or aminoazobenzene. Lignine-sulphon acid can also be coupled with diazotised bases (aniline, benzidine, β-naphthylaminedisulphonic acid), yielding azo-colouring matte This acid can also be converted into a yellowish brown nitros derivative which can be used as a dye.[65]

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[62] Lampe and Godlewoka, *Ber.*, 1918, **51**, 1347 and 1355; *J.*, 1918, 763A.

[63] *Chem. Soc. Trans.*, 1908, **93**, 489.

[64] Crabtree and Robinson, *Chem. Soc. Trans.*, 1918, **113**, 859; *J.*, 1918, 763.

[65] Oman, Eng. Pats. 103479, 103480, 103653; *J.*, 1918, 146A, 407A, 541A.

Leather waste rendered soluble by alkali is recommended for use as a dye (vandyke brown).[66]

Successive treatments of algæ with acids and alkalis lead to extracts, which may be employed in dyeing. Vegetable products (algæ, ferns, peat, tea-leaves), when heated with sulphuric acid and the solution concentrated after neutralisation with alkali, yield products utilisable in dyeing.[67]

DYEINGS PRODUCED BY METALLIC COMPOUNDS.

Closely allied to the foregoing attempts to extract dyes from sundry waste products are the efforts recently made to dye wool and even cotton by the agency of various metallic substances. These experiments will in the future always have an historical interest even if they do not lead to industrial dyeing processes, for they will serve to indicate the period when the great shortage of synthetic dyes was felt most acutely by the dye consumers. In many of these dyeings with metallic substances the wool or silk undoubtedly plays the part of a reagent.

When wool or silk is treated with the salt of a heavy metal, an alkali nitrite and an acid, and the bath gradually raised to the boiling-point, a coloration is developed on the fibre entirely different from that produced by the action of the metallic salt and acid without nitrite, and also totally different from that produced by the action of nitrite and acid followed by the addition of metallic salt. On the other hand the conjoint effect is obtained if the wool is first mordanted with the metallic salt (alone or with an assistant) and afterwards treated with nitrite and acid. Iron salts under these conditions give olive shades. Nickel gives with nitrite and a small amount of oxalic acid a salmon-pink, but with more acid a shade of tan. Cobalt furnishes olive shades. Potassium titanium oxalate gives golden yellow orange shades, fast to light. The other metals give browns, olives, and fawns. Similar results are obtained on silk.[68] These dyeings suggest the formation of co-ordination complexes in which the fibre, the metal, and nitroso- or isonitroso-groups are involved.

Wool is dyed in brown or black shades by the use of lead compounds used in conjunction with alkalis and also in combination with compounds of copper or iron. With copper and lead combinations khaki shades are produced, whereas iron and lead give rise to brown shades.

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[66] Bauer, Ger. Pat. 303599, *J.*, 1918, 407A. Allsebrook, Eng. Pat. 118735; *J.*, 1918, 649A.

[67] Malcolmson, Eng. Pats. 112474, 112813; *J.*, 1918, 120A, 145A.

[68] E. and G. E. F. Lodge, *J.*, 1916, 409.

Sulphur may be introduced into the mixture and then the dyeing effect is produced on cotton.[69]

The foregoing dyeings can be utilised alone or they may be employed in conjunction with organic dyes to which the metallic compounds impregnated in the fibres can act as mordants and developers.

With the compilation of the third and last of these reports on dyes and colouring matters which have been written during the period of the war, the author brings a congenial task to its fitting and appropriate conclusion at the dawn of peace, leaving to others the no less agreeable business of recording the great developments in this branch of applied chemistry which will undoubtedly occur in the ensuing years of reconstruction.

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[69] Malcolmson and Fitzgerald, Eng. Pat. 117095; *J.*, 1918, 502A.

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FIBRES, TEXTILES, CELLULOSE, AND PAPER.

By J. F. Briggs, A.C.G.I.

Chemist, British Cellulose and Chemical Manufacturing Co.

In contrast to the last review period, we have to record in the current year a definite increase in the output of research work both of theoretical and practical interest, while, speaking generally, the patent literature of the year shows rather a scarcity of first-class matter. In both respects these conditions reflect the general situation of the industries. The revived interest in scientific and industrial research on fundamental lines is beginning to bear fruit, and in addition to the published material, we have to remember that a vast amount of research data of the highest importance is being accumulated by the various Government departments directly connected with the war. On the other hand, the industries themselves are carrying on production under circumstances of extreme difficulty, and the surplus energies which in more normal times were devoted to improvements and inventions are now absorbed in maintaining the routine of manufacturing operations.

A noteworthy feature of recent research in the textile industries is the special attention which is being paid to physical problems which are destined to have important results on the development of the scientific and technical bases of the industries.

Fibres and Textiles.

Physical.

A research on the electrification of fibres in the mechanical preparing processes has been published by S. A. Shorter[1] in a paper dealing mainly with the electrification of wool. The electrical charge on the wool leaving the drawing frame is the resultant of positive and negative charges and of losses by conduction. The electrical effect depends on the nature of the material which is in contact with the wool. Most materials induce a positive charge on wool, and the lateral displacement of one wool fibre over another, especially under pressure, also creates a positive charge. Thus positive charges predominate in wool-spinning machinery, but certain kinds of leather, such as raw hide and so-called "oil leathers" as buff and wash leathers, electrify wool in a negative sense. Hence, such leathers when used on the delivery rollers or carding cloths have a beneficial effect in assisting the discharge of the positively electrified fibres. Asbestos, vitreous silica, and certain kinds of glass and porcelain also have a negative effect and may be usefully employed on certain portions of the machines. The systematic study of this question must infallibly lead to the mitigation of the electrification troubles in spinning mills by suitable selection of the constructional materials, and the preliminary results recorded by the author already constitute a considerable step in the direction of controlling the process.

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[1] *J. Textile Inst.*, 1918, **9**, 6; *J.*, 1918, 263A.

Another physical research of first-class importance is embodied in a communication by W. Harrison.[1] The author has investigated the optical properties of various fibres in their effect on polarised light. The double refraction of natural fibres is due to permanent strains produced by internal stresses. Strains which are also recognised by the behaviour towards polarised light may be induced by external stresses, such as strong compression or stretching. The wool fibre in particular is highly susceptible to deformation and spreading under strong compression. Stresses artificially produced by external means are easily relieved, in most cases by simple immersion in cold water or slowly by exposure to a humid atmosphere, but the natural internal stresses are only relieved by agencies which swell the fibres, *e.g.*, boiling water in the case of wool or caustic alkali in that of cotton.

These two papers are particularly worthy of note, not only because of the valuable results recorded, but because they indicate the lines on which the new era of industrial research is opening. They illustrate first the rôle which the physicist is destined to play in the development of these industries, and secondly the application of the methods and deductions of pure science to matters which hitherto had been regarded as belonging entirely to the province of the factory management and charge-hands and outside the ken of the chemist altogether. More work of a similar order is to be expected in the near future, and largely because the ground to be broken is based on practical empiricism (using the word in no derogatory sense), the results expressed in commercial terms are bound to be surprising.

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[1] *Proc. Roy. Soc.*, 1918, A, 94, 460; *J.*, 1918, 460A.

Cotton.

In a paper dealing with cotton-seed products in their relation to present day needs, E. C. de Segundo[3] draws a comparison between the British and the American methods of crushing the seed, and shows how the former will have to be modified in order to meet the conditions which demand that the economic values of the constituents be developed each to its maximum extent. The principle of the American method is the exclusion as far as possible of the seed hulls from the clean kernels, which are then utilisable, after expressing the oil, for high-grade feeding purposes, even for human consumption. About 95% of the world's production of cotton gives a woolly seed covered with an undergrowth of short fibre, and the process of separating the hulls from the decorticated kernels depends on the matting together of these woolly hulls on a vibrating sieve. The normal quantity of fluff on the seeds is unnecessarily large for this purpose, and since it absorbs oil its presence is actually undesirable. Consequently in modern practice it is usual to remove the major portion of the short seed-fibre before decorticating, leaving only just sufficient on the seed to facilitate the separation of the hulls by matting. The American system thus provides, in addition to the ordinary cotton fibre and first-grade "linters," two other fractions of commercially utilisable cellulose, namely, "cotton-seed fibre," which is the short fibre removed from the woolly seeds before decorticating and which can be delivered in so clean a state that the yield of pure cellulose approximates to that of raw cotton, and "cotton-seed hull fibre," which is the fluff taken off the separated hulls and which, though less pure, is still capable of yielding a high-grade cellulose suitable for the manufacture of explosives or paper. This is a rough sketch of the policy which will have to be applied to our Indian cotton crop after the war. The short-fibre recovery is of necessity closely associated with the oil pressing industry, and for certain economic reasons it would appear that the cotton seed products industry will have to be located and organised on a sufficiently large and concentrated scale in India itself. It is conceivable that improved machinery, established *de novo* as part of a well-thought-out and correlated scheme, may yield results surpassing those of current American practice. Segundo has studied the matter practically from the fibre-recovery end and has patented improved machinery working on novel principles for dealing with this problem.[4]

Allied to the problem of the utilisation of short cotton from the woolly seeds is the question of sorting and purifying the seedy wastes

[3] *J.*, 1918, 118T.

[4] Eng. Pats. 114435 and 114450.

or "fly" created in the scutching and preparation of cotton for the spinning process. This is mechanically a far more difficult operation because the material is far less uniform. In this connection attention may be drawn to a scheme proposed by W. S. H. Bevin[5] for the recovery of valuable spinning fibre and of residues available for cattle food from such wastes. Information is not available as to the quality of the results, but if a reasonably clean product could be obtained the operation, though on a comparatively small scale, should be commercially remunerative.

In an article entitled "Cotton sizing—an Empirical Process," R. H. Pickard[6] discusses some of the unsolved fundamental problems of the warp-sizing process, an industry of which the empirical bases have been unexpectedly attacked by the scarcity of wheaten flour. This is an operation to which exactly the same remarks may be applied as were made under the heading "Physical" in this section. No one can say why wheat flour was necessary to produce the particular results desired nor the reasons underlying the complex process of fermentation through which it has to pass in the preparation of the size. Consequently the trade was not prepared with a generally acceptable substitute. A somewhat similar position was created with regard to tallow. The research required here is one demanding high qualifications of chemist and physicist combined with the hardly-won experience of the "practical man."

Freiberger[7] discusses the question of the discoloration of bleached cotton textiles and proposes a test for the purity of cotton by noting the degree of yellow colour produced by steaming in the presence of castor-oil soap. The main cause of the yellowing in the case of bleached fabrics is the presence of oxycellulose. This last conclusion is in concordance with the experience of the present writer. In the majority of cases where degradation of colour occurs, the fabric is found to be over-bleached and to have been finished out of bleach liquor without a final sour. The yellow coloration is due to the action of basic substances, even those of the water, upon the free carbonyl groups of the oxycellulose. Freiberger's test by steaming may be a good enough test for oxycellulose, but as regards purity in other respects his observations show no conclusive differences between well scoured and badly scoured cotton.

The waterproofing of cotton canvas has been discussed by E. R. Clark;[8] the components of waterproofing compositions are classified and their properties criticised. There is probably no universal waterproofing agent, and the nature of the composition used has to be chosen according to the conditions under which the proofed fabric is expected to be utilised. The requirements in the case of canvas for military purposes are decidedly severe, and in addition to the water-repellent properties good resistance to mildew and extremes of temperature is necessary, and the capacity to stand rough usage, such as folding and friction, has also to be taken into consideration.

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[5] Eng. Pat. 110394; *J.*, 1917, 1231.

[6] *J.*, 1918, 26R.

[7] *Färber-Zeit.*, 1917, 28, 221, 235, 239; *J.*, 1918, 408A.

[8] *Indiarubber J.*, 1918, 56, 175; *J.*, 1918, 542A.

Flax and Hemp.

In the last Annual Report (p. 128) attention was drawn to Rossi's method for retting hemp and flax by substantially pure cultures of specific pectic bacteria. D. Carbone and A. Tombolato [9] have criticised the Rossi process to the effect that the characters of the resulting fibre are somewhat different from those of the standard article, the fibre bundles being more coherent and requiring special machinery for their treatment, with a tendency to produce a greater amount of tow. These differences are attributed to the use of an aërobic bacillus which is not natural to the retting process, but which was originally isolated from potatoes. Carbone's method, on the other hand, is based on the employment of an obligatory anaërobic bacillus, *B. felsineus*, which was isolated from the mud of some of the most successful natural retting pits in Italy. The process consists in steeping the hemp in artificial pits with water at 37° C., to which the selected cultures are added. The fibre produced possesses all the characters of the standard field-retted hemp, showing complete separation of the wood and spontaneous exfoliation of the bark. In comparing these two processes it must be borne in mind that the chief benefit claimed for the Rossi process was the security against the action of injurious foreign organisms which is obtained by performing the retting in the presence of a current of air, which security is not afforded by the Carbone process in an automatic manner. The Carbone process consists in the application of the principle of selected pure cultures to the ordinary retting process and its security depends only on the precautions taken to ensure the absence of inimical bacteria, whereas the Rossi process automatically excludes these forms by operating under conditions which prohibit their activity. The technical differences in the character of the fibre are admitted, and it remains to be seen whether these differences are sufficient to condemn the process from the commercial point of view.

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[9] *Bull. Agric. Intell.*, 1917, **8**, 1417; *J.*, 1918, 27A.

The patented improvements in the retting of fibre plants recorded during the year show no outstanding points of interest. B. S. Summers[10] specifies chemical retting liquors which are characterised as "alkaline baths of mitigated alkalinity." A somewhat complicated machine for decorticating retted flax has been invented by A. Meiro,[11] depending on the frictional motion of the bundles of fibre in a heated liquid, but the description suggests that the labour involved in charging the machine would discount largely the benefit obtained from the mechanical arrangement. For the preparation of hemp fibre from unretted stems, A. Colahan[12] thoroughly desiccates the raw stems in a current of dry, cool air, so that the cementing gummy matters are rendered brittle, and then removes the wood and bark by mechanical means only.

A note on the hemp industry of Korea, which is established on a substantial scale, has been published by K. Ueda.[13] The fibre is prepared by an artificial retting process and hand-scutching. The quality is excellent and the composition, according to the analysis published, is normal.

Miscellaneous Fibres.

A colour reaction which affords a differentiation between Manila hemp and all other similar rope-making fibres has been described by C. E. Swett,[14] depending on consecutive treatment with hypochlorous acid and ammonia vapour. Strands of Manila fibre are coloured russet-brown and those of other similar fibres cherry-red. The writer has not had an opportunity to examine this test, but owing to the close similarity of some of the substitute fibres to real Manila, at any rate in the raw condition, this means of differentiation should be very acceptable.

Attention has recently been turned to the preparation of fibres for coarse textile purposes from rice straw, the fibrovascular bundles being isolated, without disintegration into ultimate fibres, by restricted treatment in weak alkaline solutions. Processes of this nature have been patented by V. Volpato[15] and by J. K. Toles.[16] The search after substitute fibres in Germany continues and is reflected in patents by Pflanzenfaser Patente G.m.b.H.[17] for the production of textile fibres from plants of the lupin family, and by E. L. Fegraeus [18] for the production of a substitute for wool from *Eriophorum* fibres; these discoveries, however, are not likely to have any serious development. A far more interesting product (if the account can be relied upon) is noted in a U.S. Consular Report.[19] It is stated that a factory is being equipped in Sweden for the manufacture of peat fibre under the name of "Fiberuld." This fibre mixed with 10% of hair can be used for making felt soles. It is also employed for the manufacture of textile yarns and binding twine; moreover it is claimed that the yarn prepared from peat fibre in combination with 30–40% of wool is stronger and much cheaper than woollen yarn, and that the fabrics can hardly be distinguished from woollen cloths. So much has been claimed for peat in the past and so many fortunes have been lost in attempts at its exploitation that one is fully justified in approaching such a proposition with considerable scepticism, especially in view of the mechanically inferior structure of the peat fibre. The marine fibre (*Posidonia australis*) referred to in the last Annual Report (p. 131) would appear to be more suitable than peat for blending with wool to advantage; no further particulars, however, on its utilisation in this direction have come to hand.

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[10] U.S. Pats. 1235738 and 1238359; *J.*, 1917, 1044 and 1126.

[11] Eng. Pat. 113285; *J.*, 1918, 178A.

[12] U.S. Pat. 1233449; *J.*, 1917, 1004.

[13] *J. Chem. Ind., Tokyo*, 1918, **21**, 314; *J.*, 1918, 460A.

[14] *J. Ind. Eng. Chem.*, 1918, **10**, 227; *J.*, 1918, 236A.

[15] Eng. Pat. 113853; *J.*, 1918, 237A.

[16] U.S. Pats. 1235258 and 1262872; *J.*, 1917, 1044, and 1918, 366A.

From a report [20] dealing with the consumption of kapok in the United States, it would appear that this is undergoing an extraordinary expansion. In 1917 it was 8,500,000 lb., an increase of 45% over the 1916 consumption, while a further increase of about 35% is estimated for 1918. The bulk of the fibre is used for stuffing mattresses, pillows, &c., and only 2·8% of the total quantity is required for life-saving appliances.

ANIMAL FIBRES.

Wool.

A considerable amount of attention has been paid of late to the recovery of useful by-products, such as grease and potash, from the waste liquors from wool scouring. One of the primary essentials is to have the scouring plant so designed that the liquors are systematically enriched in the valuable by-products and are discharged at an approximately uniform concentration. The discussion of the matter has been carried a step further in a paper by R. S. Weston.[21] In order to obtain a coke from which the potash salts can be easily lixiviated, it is most important to remove the siliceous matter from the liquors, otherwise the ash consists largely of the difficultly soluble potassium silicate. For this purpose the best apparatus is the centrifugal separator, which precipitates the colloidal suspended matter. Weston expresses the opinion that it is the centrifugal machine which has rendered the recovery of potash practicable, and the grease, which is in the form of free emulsion, may also be profitably skimmed off in this machine. This conclusion coincides with that of E. V. Chambers[22] and the two papers may be read in conjunction, the former in special relation to potash and the latter to wool grease. Weston recommends heating the liquors to 60° C. and settling in a tank, re-heating to 72° C., and centrifuging (where 40–70% of the free fat may be recovered by skimming), evaporating in a triple effect plant designed specially to minimise frothing, or alternatively, by spraying in contact with hot flue gases according to the Cardem system, degreasing the concentrated liquor by volatile solvents, *e.g.* naphtha, and coking the aqueous layer in open pans. A centrifugal process very similar to the first part of the scheme described above has been patented by G. G. Jarmain,[23] a special design of continuous centrifugal separator being described. For the easy recovery of by-products there is nothing more ideal than the process of degreasing the wool by volatile solvents and then dissolving out the potassium salts by water, but although the process has been and still is operated to a very limited extent, it does not appear to find much favour in the eyes of the wool scouring trade. An article by J. H. Garner and J. F. Carmichael[24] should be consulted on the extraction of acidified sludge cakes with volatile solvents.

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[17] Ger. Pat. 302803; *J.*, 1918, 332A.

[18] Ger. Pat. 302261; *J.*, 1918, 332A.

[19] *U.S. Cons. Rep.*, July 13, 1918; *J.*, 1918, 381R.

[20] *Board of Trade J.*, Sept. 19, 1918; *J.*, 1918, 381R.

A study of the carbonising process for the removal of vegetable matters from raw wool and woollen rags has been made by W. Harrison.[25] This is a simple reaction, but the limits of chemical safety required defining with respect to the possible damage of the wool. According to Harrison's results, an initial concentration of 5 % sulphuric acid is sufficient and safe, but the hydro-extracted wool must not be heated with this acid at 100° C. for the destruction of the vegetable fibre until it has first been dried at a more moderate temperature, not above 77° C. The author has made the interesting observation that wool which has been tendered by the action of sulphuric acid may regain its strength after washing and neutralising; the wool substance is converted into a more or less colloidal condition by the concentrated acid and is again coagulated on removal of the acid. It is not contended that the other qualities of the wool remain unimpaired by this attack, and it is desirable that the duration of the stoving operation should be no longer than is strictly necessary for the destruction of the vegetable fibre. The use of formaldehyde has been suggested with a view to protecting the wool from the action of the acid by H Hey,[26] who has patented a process for the treatment of raw wool in its greasy condition. The wool is steeped in a bath containing 45% of sulphuric acid and 1% of 40% formaldehyde, centrifuged. stoved to make the vegetable matters friable, degreased by extraction with volatile solvents in a centrifugal machine, crushed between fluted rollers, and beaten in a current of air to remove the vegetable dust. A method for crushing the burrs and other vegetable impurities in stretched woollen fabrics, after heating at 77° C. to make these foreign matters brittle, has been patented by F. H. Heppleston.[27]

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[21] *J.*, 1918, 17T.

[22] *J. Soc. Dyers and Col.*, 1916, **32**, 61; *J.*, 1916, 417.

[23] Eng. Pat. 118332; *J.*, 1918, 574A.

[24] *J. Soc. Dyers and Col.*, 1918, **34**, 113; *J.*, 1918, 430A.

[25] *J. Textile Inst.*, 1918, **9**, 10; *J.*, 1918, 264A.

An anti-moth treatment for woollen goods by impregnating the fabric with a soluble salt of alginic acid and precipitating with antimony salts is worth noting.[28] K. Mohs[29] has patented a peculiar combination of Iceland moss and colloidal silicic acid, evaporated to a dry powder, for use as a fulling material.

The quantitative determination of free acidity in fabrics is always a difficult operation because of the adsorption of the acid by colloid action; it is particularly difficult with wool because the physical attraction is further reinforced by chemical affinity. The method proposed by A. Woodmansey[30] would appear to be capable of yielding useful results in certain cases where the quantities of acid present are not too small. It is based on the determination of the ratio of distribution of known quantities of standard acid between the fabric and water, as compared with a standard neutral fabric of similar quality. Curves are plotted for the two fabrics and the amount of acid already present in the sample is estimated by a comparison of the two curves.

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[26] Eng. Pat. 116763; *J.*, 1918, 409A.
[27] Eng. Pat. 100685; *J.*, 1917, 1002.
[28] Ger. Pat. 304506; *J.*, 1918, 409A. (E. Naefe.)
[29] Eng. Pat. 110343; *J.*, 1918, 146A.
[30] *J. Soc. Dyers and Col.*, 1918, 34, 172; *J.*, 1918, 541A.

Silk.

Progress in the industry of the degumming of raw silk follows two directions: the application of proteolytic enzymes, and the use of boiling-off baths of mitigated alkalinity, in the presence of dissolved colloid matters as protective agents. The principal aim of these new processes is to economise or avoid altogether the consumption of soap. E. Ristenpart[31] has investigated the chemistry of one of the simplest of the alkaline processes,[32] consisting in saturating the silk with a solution of sodium carbonate, hydro-extracting, and then steaming. He found that the reaction was perfectly sharp and required a certain definite proportion of alkali on the weight of the silk, but that the proportion of alkali required depended on the concentration of the solution, in such a way that the lower the concentration of soda solution, the smaller the proportion of alkali to silk required for effective degumming. The phenomenon is explained in terms of the ionisation of the carbonate into hydroxyl ions and bicarbonate, which is more complete the lower the concentration of the solution. In practice, the extension of the principle of increased dilution is only limited by the possibility of maintaining uniform saturation during the steaming of the goods. Within these limits the chemical reaction with the sericin can be accurately controlled without any danger of injuring the fibroin. Gebr. Schmid[33] have proposed to replace the greater portion of the soap used in the boiling-off bath by the natural lather-forming colloids formed by the action of alkali on certain waste products of the silk industry known as "gallettamini" or "pelettes," or on silk-worm chrysalides. As an example of the application of enzymes, a patent taken by Kanegafuchi Boseki[34] may be cited, according to which the raw silk is digested at 40° C. with the juice extracted from the bodies or cocoons of the silkworms for a period of 45–60 minutes.

The preservation of weighted silk goods from disintegration by external influences, by the addition of oxidisable organic substances, particularly those containing nitrogen and sulphur, has been practised for some considerable time (see Ann. Rep., II. 134) without the real chemical mechanism of the protective action being accurately understood. A similar protective effect and increase of tensile strength is now claimed in the case of non-loaded silk by treatment with derivatives of alkaloids or with products of the decomposition of alkaloids, which have a more complex molecule than urea or hexamethylenetetramine. J. Korselt[35] specifies a large number of suitable alkaloid derivatives, including salts of cinchonine and caffeine, and claims in certain cases to increase the strength of non-loaded silk by 10–50%.

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[31] *Färber-Zeit.*, 1918, 29, 181; *J.*, 1918, 649A.

[32] Ger. Pat. 291159; *J.*, 1916, 833.

[33] Eng. Pat. 107966; *J.*, 1918, 86A.

[34] Eng. Pat. 106503; *J.*, 1917, 959.

CELLULOSE.

The contributions during the past year in the domain of cellulose chemistry are quite important, and it may be stated that the field is divided between two modes of thought neither of which fully understands the view-point of the other. On the one hand we have what may be termed the old school, which envisages cellulose as a polymerised anhydride of hexose groups of large and variable dimensions. It cannot be denied that this school has the majority of adherents, and the bulk of the positive evidence. On the other hand we have the new line of thought, according to which cellulose is regarded, in virtue of its colloid character, as being in a state of ionic flux comparable with that of a solution, and it is impossible to conceive of it having a structural formula, since it is an aggregation of simple ionic groups capable of taking concrete form in a large variety of different ways according to the conditions to which it is subjected. This point of view is supported by the powerful advocacy of C. F. Cross and a certain weight of negative or circumstantial evidence which cannot be ignored. The case has been stated in general terms in the able presidential address by C. F. Cross to the Society of Dyers and Colorists,[36] and there is a promise of important results from an elaborate series of correlated researches now in progress and based largely on experimental investigations in different branches of physical science. Speculative controversies of this order are always to be welcomed on account of the stimulus they inspire into positive research. The value of a theory cannot be measured in absolute terms of right and wrong but only by the question whether it is fruitful or sterile. Many a good result has evolved from a wrong theory, if only in the process of proving it wrong. The new point of view adumbrated with respect to cellulose may be said to be at present only in its intuitive stage and cannot yet be formulated on a logical foundation, but it may lead to far-reaching consequences in our ultimate views on the constitution of the colloidal state in general.

A new step in the chemistry of cellulose has been registered by A. Pictet and J. Sarasin,[37] who have obtained through the distillation of cellulose, starch, and dextrin *in vacuo* at 200°–300° C., a very substantial quantity of a crystallisable substance, m.pt. 179·5° C., which they have identified as *l*-glucosan. The high yield (45%) of this substance supports its claim to possess some direct constitutional relationship to the parent molecule, of which it is regarded as a simply depolymerised derivative. *l*-Glucosan, $C_6H_{10}O_5$, was originally obtained by Tanret[38] from the glucosides of the *Coniferæ*; it behaves as a trihydric alcohol and yields ordinary dextrose when boiled with dilute acids. In a later paper J. Sarasin[39] proposes for *l*-glucosan the structural formula

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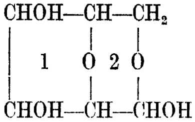
[35] Eng. Pat. 104684; *J.*, 1918, 53A.

[36] *J. Soc. Dyers and Col.*, 1918, **34**, 91; *J.*, 1918, 215R.

[37] *Comptes rend.*, 1918, **166**, 38; *J.*, 1918, 49A.



which is identical with that advanced by A. G. Green[40] for the unit complex of cellulose. Sarasin considers that in the polymerisation of *l*-glucosan the ring 2 opens, giving two free valencies for the polymerisation, since 2.5-dimethylfuran is found amongst the products of decomposition of starch and cellulose. *l*-Glucosan does not yield bromomethylfurfural when treated by Fenton's reagent, and thus differs from cellulose and starch. Hence Sarasin suggests that the ring 2 is closed in the case of the glucosan, but opens in the polymerised form. Confirmation and extension of the new data here recorded should lead to important developments. There may or may not be some connection between this simple product of destructive distillation of cellulose and the observation recorded by Cross and Bevan[41] of the formation of maltol under similar circumstances; it is at any rate an interesting coincidence that both substances had previously been isolated from pine needles.

A physical investigation of considerable theoretical interest has been carried out by S. J. Lewis[42] on the fluorescence of various types of cellulose and derivatives. This is a preliminary record of work foreshadowed by C. F. Cross bearing on the larger question of the physical properties of natural colloids. It is shown that the strength and distribution of the fluorescent properties are definite functions of the chemical constitution and are influenced in the normal manner by substituent groups. An interesting difference is recorded between the fluorescence of the normal cellulose and that of cellulose slightly modified by hydration. Acetylcelluloses exhibit an exceptionally strong fluorescence while nitrocelluloses and lignocelluloses are inactive. Physical characters so sharply differentiated must have some fundamental significance, and the development of this line of the research in relation to other physical and chemical lines will be awaited with much interest.

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[38] *Comptes rend.*, 1894, **119**, 158; *Chem. Soc. Abs.*, 1894, *i.* 564.

[39] *Arch. Soc. phys. nat.*, 1918, **46**, 5; *Chem. Soc. Abs.*, 1918, *i.* 375.

[40] *Z. Farben und Textil. Chem.*, 1904, **3**, 97; *J.*, 1904, 382.

[41] *J. Soc. Dyers and Col.*, 1916, **32**, 135; *J.*, 1916, 628.

[42] *J. Soc. Dyers and Col.*, 1918, **34**, 167; *J.*, 1918, 542A.

Celluloses of Grasses.—By a strange coincidence researches have been published, quite independently and almost simultaneously, in England and Germany, bearing almost identically on the same subject—namely, the proximate composition and constitution of celluloses of the grass family. The conclusions arrived at are almost diametrically opposed and the impartial critic has to admit that the honours of the first round appear to rest with the Germans. The English investigations have been carried out on esparto cellulose and the German on the cellulose of cereal straw, typical representatives of the industrial papermaking specialities of the respective countries.

M. Cunningham [43] starts on the hypothesis that in the work which has been held to establish the direct constitutional relationship between cellulose and dextrose, namely by hydrolysis with sulphuric acid [44] and hydrochloric acid,[45] the production of dextrose in approximately theoretical quantities has never been objectively proved and therefore the problem still remains an open one. The author, investigating the action of 72% sulphuric acid on esparto cellulose, confirmed broadly the results of Stern [46] with cotton cellulose, and obtained sulphuric acid ester derivatives, the barium salts of which contained more barium than the equivalent of the sulphuric acid combined. One of the main points of the prescription of Ost and Wilkening relative to the hydrolysis of the diluted acid liquid at 110° C. before neutralisation was, however, omitted. The failure to isolate dextrose in theoretical yield under these conditions does not justify the conclusion that "no quantitative resolution into dextrose is really obtainable." As regards Willstätter and Zechmeister's work with hydrochloric acid, the author's criticism that important constitutional questions cannot be settled by optical activities alone (especially if pentoses are present) is valid, and credit is due to her for the isolation of hydrochloric esters of the hydrolysed products; but Willstätter and Zechmeister's results had been supported by Denham and Woodhouse's[47] work on the isolation of substantial quantities of methylglucoses from methylcellulose, and it must be concluded that the previous evidence stands good until replaced by more positive data.

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[43] *Chem. Soc. Trans.*, 1918, **113**, 173; *J.*, 1918, 236A.

[44] Ost and Wilkening, *Chem.-Zeit.*, 1910, **34**, 461; *J.*, 1910, 688.

[45] Willstätter and Zechmeister, *Ber.*, 1913, **46**, 2401; *J.*, 1913, 822.

[46] Cross and Bevan, "*Cellulose*," 1895, pp. 48 *et seq.*

Dealing also with esparto cellulose, C. F. Cross and E. J. Bevan[48] have discussed the nature of the so-called "furfuroids." They show that these are selectively dissolved by moderately concentrated caustic soda and selectively hydrolysed by sulphuric acid of graduated dilution, and that in both cases there is a certain loss of total furfural by some more profound attack. It is difficult, however, to see how the authors arrive at their conclusions, since their experiments appear to support rather than weaken the view that the "furfuroids" are to be regarded mainly as pentosans.

E. Heuser and A Haug[49] have published the results of an important investigation on the action of chlorine on cereal straw and the nature of the cellulose prepared by this method. In the determination of cellulose in straw by the chlorine method, they show that satisfactory results are obtained only when a 1% solution of caustic soda at 70° C. is employed for decomposing the chlorinated material; the method of extraction by sodium sulphite does not answer in the case of straw. After four successive chlorinations of half an hour each, the cellulose is substantially free from lignin; the total amount of hydrochloric acid produced is 28·5% and the chlorine combining is 9·5–10·8%. In the treatment with chlorine, a portion of the pentosan is hydrolysed to pentose, particularly in the first treatment where the main formation of hydrochloric acid takes place; in subsequent treatments small quantities of pentosan are extracted without hydrolysis. By the action of chlorine gas on a preparation of "xylan" isolated from straw the authors found 16·8% of chlorine combined as "xylan chloride" and 16·9% converted into hydrochloric acid. In the opinion of the writer of this report the production of "xylan chloride" should not be accepted without reserve, and it appears more probable that the xylan preparation was largely contaminated with lignin. In the writer's experience with esparto, there is evidence to indicate that cold caustic soda extracts pentosan and lignin together in a state of close association which appears only to be resolved by boiling the extract. More particulars as to the purity of the xylan isolated from the raw straw are required. The authors made a complete study of the straw cellulose prepared by the chlorine method. This cellulose was obtained with a yield of 54·6 % and had a furfural value of 13·3%. The original straw had a furfural value of 15·4%; thus 47·3 % of the original xylan of the straw remained in the cellulose. This proportion of resistant pentosan is, however, a function of the severity of the extraction treatment and substantially the whole of it may be removed from the cellulose by repeated extraction with 6% caustic soda solution. Straw cellulose thus purified yields only 2% of furfural; normal cotton cellulose yields 1%, so that the separation of the pentosan from the cellulose is almost complete. It is interesting to note, in view of the writer's suggestion above, that crude straw cannot be freed from pentosan by simple extraction in the same way as straw cellulose, but that the lignin must first be removed. The results of the investigation show that straw cellulose is a mixture of normal cellulose and a pentosan, that there is no necessity to provide the latter with a special label such as "furfuroid," that the normal cellulose, freed from the pentosan, shows no constitutional differences from cotton cellulose, that it is not a "natural oxycellulose," and that on treatment according to Ost and Wilkening's method[44] it yields considerably over 90% of the theoretical quantity of dextrose.

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[47] *Chem. Soc. Trans.*, **1914, 105,** 2357; *J.*, 1914, 1084.

[48] *Chem. Soc. Trans.*, **1918, 113,** 182; *J.*, **1918, 236 A.**

[49] *Z. angew. Chem.*, **1918, 31, 99,** 103, **and** 172; *J.*, **1918, 365 and 650A.**

CELLULOSE ESTERS.

Cellulose Acetates.—The additions to the patent literature on the manufacture of cellulose acetate since the last Report are few and of little importance. W. G. Lindsay[50] treats the cellulose in a preliminary bath containing alcohol and acetic acid before acetylation with a mixture of acetic anhydride and benzene. F. Ruppert[51] employs a metalloid chloride as catalyst and avoids the solution of the reaction product, converting the cellulose into a non-liquefied jelly without, however, using anything of the nature of a non-solvent diluting agent. The product is soluble in tetrachloroethane but not in glacial acetic acid. According to a process by G. J. Esselen, jun., and H. S. Mork[52] cellulose is acetylated without destroying its fibrous form, and the product is dissolved in acetic acid containing a catalyst until the desired degree of solubility in acetone is reached. The trend of recent invention is in the direction of endeavouring to find a practicable process of acetylation with preservation of the fibrous form, as in the manufacture of nitrocellulose. Certain advantages as regards cleanliness, the use of a cheaper raw material, and uniformity of acetylation

[50] U.S. Pat. 1265216; *J.*, 1918, 461A.
[51] U.S. Pat. 1263119; *J.*, 1918, 367A.
[52] U.S. Pat. 1275884; *J.*, 1918, 651A.

are offered by such processes but, as at present developed, the use of non-solvent diluents introduces too many complications to constitute an attractive commercial proposition.

The chemistry of the acetylcelluloses still awaits a rational co-ordinated statement. The literature of the subject is almost entirely confined to patent specifications drawn up by legal and commercial minds and designed to suppress rather than develop the scientific principles which govern the relations existing between the various forms of product. These relations when reduced to plain terms are by no means so chaotic as would appear from a review of the published data, but at the same time, quite a number of partially obscure problems remain to be worked out by disinterested research before the subject can be rescued from the hands of the empiricists.

Solutions and Plastics.

The process of "doping" the fabric of aeroplane wings is an operation which has always been performed by hand. An arrangement which is intended to carry out the doping of the planes by mechanical means has been devised by W. B. Makins,[53] who employs, in a closed box, travelling spraying devices mounted on a reciprocating carriage and adapted to deliver slightly overlapping bands of coating liquid. The successful introduction of mechanical doping would be of immense benefit to the industry, but it is to be feared that the absence of the personal factor would restrict the use of the machine in many respects. The hygienic aspect of the doping industry is dealt with in a report by the Inspector of Factories and Workshops,[54] and valuable recommendations are made as regards ventilation. It is satisfactory to note that, although the industry was working at very high pressure in 1917, only eleven cases of dope poisoning were notified, all of these being traced to faulty ventilation.

There is nothing new to be added to the list of the known plastifying agents used or proposed for the preparation of cellulose acetate masses. A number of patents have been published during the year, but as the agents specified have already been covered several times over, no useful purpose would be served by enumerating them; the matter may be left to be fought out by the patent experts.

Other Plastic Materials.—Attention may be directed to processes for the manufacture of transparent masses resembling celluloid from vegetable proteins, patented by S. Satow.[55] The proteins are "glutinised" either by an alkaline salt, such as sodium sulphite, or by an acid, and the mass is combined with an active methylene compound or with an oxymethane sulphonic derivative. Further developments of the patents of H. Blücher and E. Krause[56] are also of interest, relating to the manufacture of plastic masses resembling horn or ebonite from the material produced from waste yeast and formaldehyde. Products prepared from previously dried yeast have different properties from those obtained by the action of formaldehyde on moist yeast; modifications are also introduced by different methods of mixing and by the incorporation of tar or tar oils.

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[53] Eng. Pat. 113844; *J.*, 1918, 237A.

[54] Cd. 9108; *J.*, 1918, 307R.

CORK SLABS.

H. Ost[57] has investigated the process of the manufacture of compressed slabs from pulverised cork waste. The cork is placed in moulds and then heated under compression at 160°–180° C. The mechanical strength of the slabs depends on the degree of compression and the temperature and time of heating. No binding agent is used and the author's experiments with raw and extracted cork waste dispose of the suggestion that the natural resinous matters of the cork play any part in cementing the particles together. The resistance to disintegration by water or steam is almost entirely a function of the temperature of heating under compression, and if the slabs are only moderately heated they disintegrate immediately when wetted. The author's explanation is that the solidity of the slabs is due simply to the interlocking or felting of the cork cells, and that the process of heating at 160°–180° C. induces incipient decomposition, so that the elasticity of the cork is not restored on steeping in water and the compressed mass remains permanent and rigid. This explanation appears to be perfectly feasible, but there remains room for further investigation on the nature of the physical change which is induced in the cork substance by heating and which renders it incapable of swelling in water. The author's experiments show that there is no exudation of fatty or resinous matters, but it is not sufficient to say simply that the cork loses its elasticity, as in that case one would expect the slab to soften in water like a pulp board.

[55] U.S. Pats. 1245975, 1245976, and 1245983; *J.*, 1918, 27A.

[56] Ger. Pats. 302930, 302931, and 303133; *J.*, 1918, 478A.

[57] *Z. angew. Chem.*, 1918, 31, 105; *J.*, 1918, 409A.

ARTIFICIAL TEXTILES.

Artificial Silk.—H. Ost [58] has made some very interesting studies on the formation of the thread in the spinning of cuprammonium silk from glass capillary jets. The cellulose solution is instantaneously solidified when the coagulating liquid comes in contact with it; there is no plasticity of the solid and any "drawing down," *i.e.* difference between the diameter of the capillary and that of the wet thread, is produced by a tension acting upon the fluid cellulose. The tension is determined by the relation between the speed of spinning and the supply of cellulose solution, and the latter depends on the feed-pressure and the internal resistance of the jet, which in its turn is a function of the length and diameter of the capillary. Certain optimum relations have been established between these various factors. In spinning cuprammonium solutions the normal size of the capillary is 0·2 mm., from which threads of 0·1 mm. can be obtained having a diameter of 0·03 mm. when dry. When the speed of drawing tends to exceed the speed of delivery, the point at which the reduction of diameter takes place recedes up the capillary and the coagulating liquid enters the jet as far as this point. It appears that the limits of reduction in the diameter of the thread are restricted by practical considerations, among which one of the most important is the frictional resistance of the jet, and capillaries of less than 0·2 mm. diameter do not afford correspondingly finer threads without risk of frequent breakage. From the above observations it will be understood how closely the industrial factors of spinning depend on the physical tenacity or cohesive quality of the cellulose solution, which in turn is a function of its chemical quality. Although, in the process of spinning from capillary jets into a powerful coagulating bath, there is no plasticity of the thread once it is formed, Ost is careful to point out that in the Thiele process, where a weak coagulating bath is employed, the solidification of the thread is not instantaneous, and by graduated tension on the semi-coagulated thread after it issues from the spinning orifice it is possible to stretch it out to very much finer diameters than are obtainable in the other processes.

M. de Chardonnet [59] describes the physical factors which determine the contours of the cross-sections of collodion artificial silks. If these are produced by coagulation in liquids, a relatively dilute solution of pyroxylin is employed. The circumference of the coagulated thread is permanently fixed immediately on issuing from the jet, and the coagulum being relatively dilute, the subsequent shrinkage on drying is large and results in a shrivelling, which produces threads having cross-sections with more or less star-shaped contours. For spinning by evaporation, very highly concentrated solutions of pyroxylin are employed and the circumference of the thread is not fixed before the interior has solidified; the cross-sections of such threads have a kidney-shaped contour. For practical reasons collodion silks are manufactured mainly by the latter process, and although their "covering power" is less than that of the more irregular coagulated thread, it is sufficiently good to give satisfactory results. Chardonnet points out that it is possible, even by the coagulating process, to produce perfectly cylindrical threads by spinning into dilute alcohol, which prevents the hardening of the surface layer and allows it to shrink at the same rate as the interior of the thread. A close study of the cross-sections of artificial silk throws the strongest light on the physical conditions of thread formation and therefore is a most characteristic guide to the identification of different spinning systems. The cross-section is modified by several factors in the mechanical arrangement of the plant, and the recognition of abnormal cross-sections is one of the most important points in the control of the process. The influence of the cross-section on "covering power" is obvious, and the connection between the shape of the thread and its reflected lustre has also to be studied.

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[58] *Z. angew. Chem.*, 1918, **31**, 141; *J.*, 1918, 542A.

[59] *Comptes rend.*, 1918, **167**, 489; *J.*, 1918, 650A.

The same author[60] has communicated some details on the composition of effluents from collodion silk factories. He advises the partial neutralisation of the liquors by mixing the washings from the denitration of the silk with those from the nitration of the cotton in a closed tank and completing the neutralisation with lime. Free sulphur is precipitated and the neutralised solution contains calcium nitrate equivalent to 0·65 grm. of HNO_3 per cub. m.

E. Barbet et Fils et Cie.[61] have patented a process and apparatus for the recovery of ether and alcohol vapours from air by absorption in diluted sulphuric acid and distillation in a column still.

Paper Textiles.—An article in the Board of Trade Journal[62] deals with the manufacture of paper yarns. Two processes appear to be in use, namely spinning on a modification of a ring frame machine and spinning from rotating pans (Tellerspinnmaschine). Improvements on pre-war models appear to be rather in matters of detail than in principle. Great advantages are claimed with respect to the results obtained by the use of certain impregnating solutions, but the products still remain very sensitive to water. In a subsequent article[63] the economic development and outlook of the industry are discussed. The output of paper yarns in Germany and Austria at the end of 1917 was estimated at the rate of 200,000 to 300,000 tons per annum, and this material has saved the majority of the textile factories from being closed down. After the war paper yarns may come into serious competition with jute, and although they present, as regards durability, many points of inferiority, it is to be expected that strong efforts will be made to foster the vested interests in the home industry which have been created. Questions of cost of production and shipping facilities will determine the situation in respect to jute, and it is quite possible that for certain definite uses paper textiles will fill a permanent position on the world's markets. The writer has inspected some of the most recent samples of these fabrics, which may be classified as coarse textiles made from strong "Kraft" brown papers and finer textiles made from white papers. Both types lend themselves readily to dip-dyeing and colour printing, and some of the latter specimens are extremely effective when viewed at a slight distance. Even the finest of the fabrics is nothing more than a dismal failure for clothing purposes and that application cannot be expected to survive the period of stern necessity. On the other hand, fabrics for use as curtains, hangings, and perhaps tablecloths, which do not have to undergo much handling, can be produced with very artistic effects.

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[60] *Comptes rend.*, 1918, **166**, 783; *J.*, 1918, 366A.
[61] Eng. Pats. 101723 and 101875; *J.*, 1918, 45A.
[62] *Board of Trade J.*, Feb. 14, 1918; *J.*, 1918, 106R.

Paper yarns are generally sold in a moist condition carrying 40–80 parts of moisture per 100 of dry substance, and M. Lummerzheim[64] communicates some observations on the damage which may occur if the goods are permitted to freeze during transport or in the weaving shed. If the yarns are already frozen, the thawing must be performed very gradually. Note may be taken of methods for cleaning and renovating paper textiles as described by T. Goldschmidt.[65]

WOOD.

The study of the chemistry of wood substance, noted in the last Annual Report (page 144), has been extended by A. W. Schorger,[66] who has developed a method for the determination of mannan in wood and other plant substances by hydrolysis with hydrochloric acid and precipitation of mannose phenylhydrazone. Coniferous woods contained from 1·44 to 9·22% of mannan, but the hard woods examined were free from it. The proportion of mannan is usually greater in the sap-wood than in the heart-wood and it decreases from the base upwards.

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[63] *Board of Trade J.*, Sept. 12, 1918; *J.*, 1918, 376R.
[64] *Monatschr. Textil Ind.*, 1917, 32, 144; *J.*, 1918, 408A.
[65] Ger. Pats. 305427 and 306000; *J.*, 1918, 410A and 575A.
[66] *J. Ind. Eng. Chem.*, 1917, 9, 748; *J.*, 1917, 1003.

Attention was directed last year to the very important paper by Schorger on the analytical investigation of wood, and we have to record an equally important study by B. Johnsen and R. W. Hovey[67] communicated to the Canadian Section of this Society. This is all really first-class matter carefully worked out; it should be considered carefully side by side with Schorger's work and the best features of each should be "averaged." It is impossible to do justice to the contents in the space available here and the few comments which follow should not be taken to indicate any lack of appreciation of the work. In the determination of cellulose by the chlorination method the initial dominating factors are the mechanical disintegration of the sample and the subsidiary chemical treatments designed to remove matters other than the true lignin. As regards the mechanical preparation, the matter is not even yet so simple as could be desired. The authors recommend a very fine subdivision of the sample in order to obtain a perfect reaction between the gas and the solid; the wood is to be powdered so as to pass an 80-mesh but not a 100-mesh sieve. This entails a very severe disintegration of the fibre substance and involves working with a very small quantity of the sample for the analysis, to avoid filtration difficulties. The authors apparently do not recognise the importance of using the entire ground sample and the danger of getting a fractionation in composition during sifting, owing to the separation of the more friable from the tougher portions of the wood. As regards the chemical preparation of the sample for chlorination, the authors introduce a novelty by submitting the wood to a preliminary digestion at 135° C. with a mixture of acetic acid and glycerin. This treatment, as the examples given in the paper show, removes some of the more readily hydrolysable carbohydrates, notably pentosans and probably hexosans, and thereby lowers the yield of cellulose by 3–4%. If it afforded a sharp cut between clearly differentiated groups of constituents, this proposed treatment could be more readily accepted. As it stands, the principal argument in favour of it is that the reduced yields of cellulose and furfural more nearly correspond with those obtained in commercial wood pulps. This argument is one of expediency and not of principle and does not appeal strongly to the scientific mind.

The authors have studied the nature of the attack of fungi resulting in the formation of "touchwood." The decayed wood showed a loss of cellulose and pentosan, with a resulting concentration of lignin and methylfurfural matters, and a large increase in the water-soluble substances. This result agrees closely with the observation of R. E. Rose and M. W. Lisse.[68] An interesting feature of the investigation is the use made of Klason's method of determining lignin as the residue insoluble in 72% sulphuric acid. This method is regarded as satisfactory in the case of spruce and the coniferous woods generally, but seems to fail entirely to give reasonable results in the case of aspen and the "hard" woods, whence it is concluded that the latter group of woods contains a lignin of a different type. With regard to the substances which yield methylfurfural, these researches confirm the exceptional power of resistance of those constituents, both to acid hydrolysis and to attack by fungi; in both cases the methylfurfural value moves with the lignin rather than with the furfural. Thus, although the available evidence points clearly to an identification between the furfural value and pentosans, there are not the same grounds for concluding that the methylfurfural value represents methylpentosans. There is a general agreement that the methoxyl value is directly derivable from the lignin component of the wood, but its use as a measure of the lignin should be accepted with caution. Already, as mentioned above, there is a suggestion of the existence of more than one type of lignin, and this view receives positive confirmation in a research by M. Honig and J Spitzer,[69] who have isolated from sulphite waste liquors from coniferous wood two lignosulphonic acids, one containing four times as much methoxyl as the other. C. G. Schwalbe,[70] in advocating the desirability of co-ordinating the lines of development of analytical researches of the kind now under discussion and the standardisation of the methods, appears to suggest that the results for methoxyl value should be corrected by those for the methylfurfural in order to arrive at a measure of the lignin, but the writer cannot admit that any such connection between the two types of CH_3 groups can be assumed to exist.

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[67] *J.*, 1918, 132T.

C. G. Schwalbe and W. Schulz[71] record the fact that pine wood contains 11·4% of crude resin containing 2·7% of fatty acids; the greater portion of this resin is concentrated in the dark-coloured heart wood, which gives 16% of crude resin with 3·5% of fatty acids, while the sap wood gives only 2·4% of resin with 1·2% of fatty acids.

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[68] *J. Ind. Eng. Chem.*, 1917, **9**, 284; *J.*, 1917, 457.

[69] *Monatsh. Chem.*, 1918, **39**, 1; *J.*, 1918, 502A.

[70] *Z. angew. Chem.*, 1918, **31**, 193; *J.*, 1918, 685A.

[71] *Chem.-Zeit.*, 1918, **42**, 229; *J.*, 1918, 382A.

WOOD PULP.

In view of the importance of combining the resin and turpentine industry with the wood pulp industry wherever the conditions are favourable, attention should be directed to experiments carried out by O. Kress and C. K. Textor [72] on the digestion of chips of longleaf pine which had been treated for the extraction of the resin and turpentine. The yields of "Kraft" pulp obtained ranged from 35·3 to 43·8% and a further recovery of oil amounting to 2·3 galls. per ton of chips was recorded. The strength of the paper produced from this material was inferior to that from fresh wood, but since the extracted pine chips represent a waste material used only for fuel, its conversion into paper should constitute a decided technical advance.

A research of some considerable interest has been published by T. Marusawa,[73] dealing with the constitution of various bisulphite solutions and their stability at various temperatures. The conditions under which the sulphurous acid decomposes into sulphur and sulphuric acid have been studied. Under parallel conditions the stability of the liquor decreases as the ratio of free sulphurous acid to bisulphite is increased. The decomposition of sulphurous acid is accelerated by hydrogen ions and the catalytic action of selenium may be explained by the assumption that it forms with HSO_3' an unknown compound which is exceedingly unstable in the presence of H-ions.

There have been several additions to the patent literature of the digestion process during the past year, but it is difficult to say that any of them stand out as marking a new departure of fundamental importance. The trend of invention is towards modifying the severity of the action of the liquor on the cellulose and making provision for the collection of resins, turpentine, and oily by-products. One of these patents deserves mention if only for the novelty of the idea: Aktiebolaget Cellulosa [74] proposes to carry out the digestion of wood with caustic soda without sodium sulphide in the presence of a contact substance favouring reduction, and it is suggested that the interior of the digester be coated with mercury for that purpose. The caustic lye is employed at only half the usual concentration.

One of the most interesting lines of modern development in the manufacture of pulp is the principle of fractional digestion. Reference was made to this in the last Report (p. 148) in connection with Raitt's process for the digestion of grasses. C. Ziegelmeyer [75] describes the working of a similar principle with wood pulp according to Ungerer's process. The fresh wood is treated at a moderate temperature with a nearly spent alkaline lye, which removes the readily alterable carbohydrates and sugars without the formation of dark-coloured decomposition products. It is the products formed from these carbohydrates at a high temperature that cause the dark colour characteristic of pulps digested by the alkaline process. If the carbohydrates can be removed without serious caramelisation, the fibres remain unstained and the lignin may subsequently be attacked by a clean fresh liquor at as high a temperature as is necessary and yield a pulp which approaches sulphite pulp in colour. This liquor containing only lignin has no staining properties and is passed on through the battery of digesters in contact with fresher wood until the alkali is saturated. The process is being worked on the large scale at a Continental mill and arrangements are in hand for large extensions.

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[72] *J. Ind. Eng. Chem.*, 1918, **10**, 268; *J.*, 1918, 296A.

[73] *J. Chem. Ind., Tokyo*, 1917, **20**, 737; *J.*, 1918, 52A.

[74] Eng. Pat. 116288; *J.*, 1918, 651A.

[75] *Papier-Zeit.*, 1918, **42**, 1855; *J.*, 1918, 408A.

For destroying the evil-smelling waste gases from the digestion of pulp by the alkaline sulphide process the Zellstoff-fabrik Waldhof [76] proposes to lead them directly to the primary air-intake of the gasifying chamber of a fuel gas producer, so that they pass through the entire combustion zone and any products which escape combustion there have a second chance of being burnt when the fuel gas is used.

Testing.—For distinguishing between bleached and unbleached sulphite pulps, G. Bright [77] recommends Cross and Bevan's ferric ferricyanide reagent as a microchemical stain, the contrast being enhanced by cross-staining the bleached fibres with Congo Red. P. Klemm [78] bases the distinction between sulphite and soda pulps in paper first on the staining of the resinous contents of the medullary ray cells in sulphite pulp with an aqueous alcoholic solution of Sudan III, and secondly on the strong reaction of the contents of the pitted pores of the sulphite pulp fibres with a solution of rosaniline sulphate mixed with a little alcohol and sulphuric acid.

Waste Liquors.

In a paper contributed to the Canadian Section, B. Johnsen[79] gives an excellent review of the present position of the waste sulphite liquor problem. Passing over a number of trivial uses to which the organic matters of the spent lyes could be applied, it is satisfactory to note that the author recognises that nothing short of a really large self-contained scheme is worth the consideration of an industry of this magnitude. The most important of the minor applications of spent sulphite liquor is as a tanning adjunct, and this application appears to have "made good" so far as the relatively limited demand can be expected to extend. Of the larger schemes, that for the production of alcohol from the fermentable sugars has already attained commercial importance in Norway and Sweden, and is being developed on an extensive scale in Germany and other pulp-producing countries. The average yield of alcohol on a commercial scale amounts to 1% on the volume of the liquor, but is capable of expansion up to 1·25%. The manufacture of alcohol, however, accounts for only a fraction of the total organic solids of the liquor, and the main problem still remains unsolved when it comes to dealing with the spent wash. Strehlenert's process [80] for the recovery of a fuel, having a calorific value of 6000 cals., by precipitation of the lignin derivatives, is stated to be in operation in Scandinavia and to be undergoing considerable development there, although the economic factors do not appear to be in its favour in America. According to this process sulphuric acid is produced in the liquor itself, according to the equation $3SO_2 = S + 2SO_3$, by heating the liquor in lead-lined autoclaves at a high temperature in the presence of air under high pressure. The sulphuric acid thus produced causes the precipitation, under favourable conditions of concentration of the liquor, of 75% of the organic solids, which are regarded as existing in the form of sulphinic acids, whilst the remaining 25% exist as sulphonic acid compounds. The question of submitting the precipitated lignin derivative to destructive distillation for the recovery of methyl alcohol, acetic acid, and other wood-distillation products has received consideration and would appear to offer more attractive prospects than its direct use as a fuel. This aspect, however, has not yet been investigated sufficiently to enable the commercial results to be accurately ascertained, particularly with regard to yields and purity of the respective products; it is, in fact, quite possible that the major portion of the acetic acid component of the wood is not in the precipitate at all. H. B. Landmark [81] has patented a process for inducing the precipitation by the discharge of electric sparks in the presence of oxygen or air under pressure, with the object of employing the precipitate as a fuel, and I. Sörass [82] proposes to perform the treatment at a lower temperature, but still under high pressure, by heating the liquor first at 80° C. in an atmosphere deprived of oxygen and secondly at 100° C. in the presence of air until the lignin is precipitated. The oxygen of the air is absorbed by the liquor in the second stage and the exhaust gas may serve as the non-oxidising atmosphere for the first stage of the following charge.

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[76] Eng. Pat. 115350; *J.*, 1918, 367A.

[77] *J. Ind. Eng. Chem.*, 1917, **9**, 1044; *J.*, 1918, 5A.

[78] *Wochenbl. Papierfab.*, 1918, **48**, 2159; *J.*, 1918, 408A.

[79] *J.*, 1918, 129T.

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[80] Ger. Pat. 266096; *J.*, 1913, 1104; and Ger. Pat. 308144; *J.* 1918, 764A.

[81] U.S. Pat., 236948; *J.*, 1917, 1092.

[82] U.S. Pat. 1268774; *J.*, 1918, 543A.

In a Board of Trade report[83] it is stated that the production of alcohol from four sulphite pulp factories in Sweden amounts to 3,000,000 litres per annum; several new alcohol plants are in course of erection.

One of the principal obstacles to all propositions for the utilisation of waste sulphite liquors is the cost of evaporation to a suitable consistence. Even in the precipitation process, the treatment should be carried out at a favourable concentration of organic solids (about 17%) in order to obtain the best results, the original concentration being about 10%. E. Oman[84] recommends concentration by freezing instead of by evaporation, either before or after the fermentation. The ice crystals are removed in centrifugal machines, and by repeated freezing a liquor containing 35% of dry solids may be produced without injury to the sugars. In Scandinavia, where water power is available, it is stated that the cost of removing a ton of water by freezing is only one-tenth of that required for evaporation.

The foregoing summary shows that considerable progress has been made in dealing with the sulphite waste liquor problem and that this problem is being handled no longer on the lines which had for many years been followed, but on a scale more commensurate with the importance of the industry.

E. Oman[85] states that sulphite liquors with 10% of dry substance contain, in addition to 2·5% of sugar, 2·5% of calcium "lignin" sulphonates and 5% of calcium "lignone" sulphonates. The "lignin" sulphonates are precipitated by saturating the liquor with common salt and heating to 50°–70° C., while the "lignone" sulphonates remain dissolved even after concentrating the saturated liquor to one-sixth of its original bulk. In a series of several patents, E. Oman[86] proposes to separate these two groups and seeks to utilise them as chemical products by converting them into various derivatives, *e.g.* hydroxylignin and hydroxylignone by fusion of the sulphonates with caustic alkali, nitro- and nitroso-derivatives of the sulphonates applicable as colouring matters. The lignin or lignone sulphonic acids or salts may be employed for coupling with diazotised primary amines to produce azo-dyestuffs.[87]

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[83] *Board of Trade J.*, July 18, 1918; *J.*, 1918, 321R.

[84] *Papierfab.*, 1918, 15, 605; *J.*, 1918, 409A.

[85] Eng. Pat. 106493; *J.*, 1918, 461A.

[86] Eng. Pats. 103649 to 103655 and 106493; *J.*, 1918, 121, 146, and 461A.

[87] Eng. Pats. 103479, 103480 and 103822; *J.*, 1918, 407, 541, 573A.

In connection with the treatment of spent lyes from the digestion of wood by alkaline processes, the main obvious line of development is the recovery of methyl alcohol, acetone, and acetic acid by destructive distillation, and lixivation of the charçoal for recovery of the alkali. The chief present obstacle is the engineering difficulty to devise a suitable plant, preferably for continuous operation (see Ann. Reports, vol. ii. 146). W. Schacht[88] has designed a plant for the production of acetone, oils, and nitrogenous compounds from cellulose waste lyes by spreading the material in thin layers on trays in a battery of interconnected vertical retorts.

Straw.

The past year has witnessed the revival of the manufacture of straw pulp in British paper mills as a direct consequence of war conditions, first to replace the restricted importations of Continental yellow strawboards, and secondly to substitute a home-grown raw material for the imported esparto grass which was the mainstay of a number of the fine writing and book paper mills. Both movements were brought about by the necessity for saving tonnage. A still stronger necessity has more recently arisen which promises temporarily to restrict or inhibit the use of straw as well as esparto for the manufacture of fine papers, namely the necessity of economising coal. When conditions become easier, the question of the continuation of the manufacture of British strawboards will be a matter of relative cost of production, while in the case of the fine paper mills esparto may be expected to be restored to its former position on the ground of merit, although a revival of food-cultivation in this country would place straw in a more favourable position than it has occupied in the past. A patent by E. J. Luppen,[89] for digesting straw with water under pressure and removing the liberated gummy matters by displacement with cold water, indicates a step in the direction of producing the cheaper grades of strawboard without chemicals.

Experiments have been carried out at the Imperial Institute[90] to determine the value of rice straw for paper-making. This straw possesses the advantage of giving a fibre of high quality for paper pulp with an unusually low consumption of soda, but this advantage is partly counterbalanced by the losses in the recovery of soda from a material so rich in silica. The pulp bleaches easily and gives an excellent paper.

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[88] Ger. Pat. 303053; *J.*, 1918, 322A.

[89] U.S. Pat. 1236723; *J.*, 1917, 1092.

[90] *Bull. Imp. Inst.*, 1918, **16**, 16; *J.*, 1918, 601A.

A U.S. Consular Report[91] deals with the Tunisian alfa or esparto grass industry. Before the war the imports to the United Kingdom were made up of 100,000 tons from Algeria, 45,000 from Spain, 30,000 from Tunis, and 30,000 from Tripoli—a total of 205,000 tons, representing 92,250 tons of paper.

Miscellaneous Fibres.

An interesting development in the manufacture of pulp from plant materials which are not highly lignified is described in a patent by C. Beadle,[92] who proposes to treat materials such as green, freshly cut *Hedychium coronarium* or cotton hull fibre, directly in the beating engine with hot caustic soda solution, in order to carry out simultaneously the chemical and mechanical disintegration of the material. In many cases the proportion of alkali may be so restricted that it is completely neutralised by the acid products of the reaction. This principle appears to be capable of considerable extension, with distinct saving in chemicals and steam, and it is well worth noting for the purpose of simplifying the treatment of strong materials for the manufacture of unbleached papers. A process for utilising dead leaves has been proposed by K. Bramson,[93] who separates the veins and ribs for the preparation of paper pulp and utilises the powdered blades for the preparation of cattle fodder or for the recovery of by-products by destructive distillation. A somewhat similar proposition is contained in a patent by W. T. Moore[94] for the utilisation of bracken for paper-making. The leafy parts are stripped from the fronds by drawing them through an aperture in a frame, and the soft portions are digested with water while the hard stems are treated with caustic soda; the two materials are mixed together after digestion and reduced to pulp. Propositions of the above nature, however, can only be regarded as war-time makeshifts, as the bracken fibre is too short and the cost of isolating it is too high to make it attractive when other materials are obtainable. The perennial problem of the utilisation of cotton stalks forms the subject of a patent by L. D. Jones;[95] but this cannot be regarded as bringing this problem any nearer a practical solution.

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[91] U.S. *Cons. Rep.*, Apr. 3, 1918; *J.*, 1918, 301R.
[92] Eng. Pat. 116005; *J.*, 1918, 409A.
[93] *Comptes rend.*, 1918, 166, 853; *J.*, 1918, 366A.
[94] Eng. Pat. 118291; *J.*, 1918, 575A.
[95] U.S. Pat. 1257080; *J.*, 1918, 238A.

Waste Paper.

The war has brought the waste paper industry to the forefront, and even in a humble sphere such as this there is room for the application of scientific principles. The systematic classification of the various grades of the collection is an instructive exercise in the conservation of values, and the appropriate cleaning and re-manufacture of these grades presents problems which are by no means at the stage of complete development, either mechanically or chemically. It is satisfactory therefore to note the publication of a text-book by J. Strachan[96] devoted entirely to this subject, and it is safe to predict that the recognition it has now received will ensure definite and remunerative progress. An arrangement for pulping waste papers and for washing the pulp on an inclined screen, which has been patented by the Société Union Française des Papeteries,[97] should be noted, but the washing arrangement appears rather wasteful. A process patented by J. Galloway and A. Stratton[98] presents no points of novelty.

PAPER MANUFACTURE.

Statistical.

R. W. Sindall, according to the report of a lecture given at the London School of Economics,[99] has calculated, from what statistics are available, the approximate effects of the war on the production of the British paper mills, and gives figures illustrating the adjustments which have been rendered necessary. Classified details are given of imported papermaking materials contrasting the years 1914 and 1917, and an approximate estimate is deduced for the reduction in the manufacture of paper. It is suggested that the home manufacture of paper declined from about 1,050,000 tons in 1914 to about 650,000 tons in 1917.

Machinery.

E. Partington[100] has described a connected system of several hollander beating engines for the beating of paper pulp in a single passage through the system, taking advantage of the fact that pulp fed in at one side travels several times round the trough before it reaches the outer side from which it is discharged into the next beater of the series.

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[96] "*The Recovery and Remanufacture of Waste Paper*"; *J.*, 1918, 403R.

[97] Eng. Pat. 114257; *J.*, 1918, 264A.

[98] Eng. Pat. 115940; *J.*, 1918, 409A.

[99] *J.*, 1918, 167R.

[100] Eng. Pat. 110482; *J.*, 1917, 1232.

The substitution of the suction roll for the couch press has had a definite though limited measure of success. An improvement in the principle of the suction roll has been devised by G. Hellström[101] with a view to keeping the perforations of the roll clear of deposits by the washing out action of the water withdrawn from the paper. In this device the suction box, instead of being situated inside the roll, is placed on the outside underneath, and exerts its suction on an internal stationary chamber inside the roll which is isolated from the atmosphere by packing pieces. The water from the paper enters the upper segment of the roll and passes out into the suction box through the perforations in the lower part. C. E. Pope[102] describes an arrangement for continuing the wire beyond the couch press by passing it over a positively driven end-roll and blowing off the web of paper by a blast of air beneath the wire between these points. A novelty in the method of varying the inclination of the wire of the paper machine is embodied in a patent by J. Alpine,[103] according to which the frame is pivoted at the breast-roll end and raised or lowered at the couch-roll end, having a take-off arrangement working in conjunction with an extra suction box acting on the felt.

A mechanism for automatically controlling the steam supply to the drying cylinders, which is operated by the tension of the moist paper passing through the drying system, has been devised by C. Stickle.[104]

Special Papers.

Engineers' "Blue Prints."—A very important article has been published by F. P. Veitch, C. F. Sammet, and E. O. Reed[105] on the specifications of composition and qualities required for the paper used for the photograghic reproduction of engineers' drawings. The specifications demanded by the authors appear to be rather severe, and good blue-print work is being done on much cheaper papers, but there is no doubt that the qualities required by the consumer—namely, capacity to withstand rough and rapid handling in the developing baths and hard wear and repeated folding when in use—are such as are imparted to the fullest extent by the use of sound, well-beaten rag stock. The two special tests for quality are the folding resistance and the tensile strength in the wet condition; these standardised tests afford indications of durability. In the case of blue prints the quality of the finished print is equal to that of the original paper, but in the case of brown prints the acid sensitising chemicals bring about a decided deterioration in the wearing quality of the prints. The manufacture of a suitable paper depends not only on the use of materials of high quality, but also to a very great extent on the beating of the fibre and its manipulation on the machine, so as to obtain a flexible well-felted sheet. Tensile tests for strength in the wet condition are made on strips 15 cm. wide after steeping in water at 21° C. for twenty minutes.

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[101] Eng. Pat. 105556; *J.*, 1917, 1269.

[102] U.S. Pat. 1257737; *J.*, 1918, 238 A.

[103] U.S. Pat. 1275826; *J.*, 1918, 652A.

[104] Eng. Pat. 113240; *J.*, 1918, 178A.

[105] *J. Ind. Eng. Chem.*, 1918, 10, 222; *J.*, 1918, 237A.

Metallised Transfer Paper.—According to a patent by F. Tscheike,[106] metal foil is attached to paper by coating the paper with an adhesive which becomes sticky at a high temperature and then pressing the metal foil against the coated paper on a heated support by means of a cooled roll. The metal foil may be transferred in an embossing press by coating the surface of the metal with an adhesive of greater strength than the first, so that under the pressure of a heated die the metal foil is released from the paper and adheres to the article to be embossed.

Waterproof Paper.—B. Kniffler[107] claims the use of an emulsion of paraffin wax and an aqueous solution of an ammonium soap as a coating for paper to make it waterproof.

Paper Containers.—There is bound to be a great expansion in the use of paper or cardboard containers in place of tins and glass or stoneware jars after the war, both on account of lightness and cheapness. These containers are generally dipped in melted wax, but attention is being devoted to the search for effective substitutes which may offer some points of advantage. In this connection a patent by L. Buchbinder[108] should be noted, in which a glue-tannin precipitate is mixed with a decoction of Iceland moss or with a concentrated alcoholic solution of resin and the liquid is used in combination with a mineral filler. Another combination of a somewhat similar order is described by P. Poetschke[109] and is intended for making phonograph records. Fibre sheets, which may be perforated, are incorporated together to form a laminated mass by means of a mineral cement, for instance magnesium oxychloride cement, together with silex, and the compounded body is pressed.

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[106] Eng. Pat. 113297; *J.*, 1918, 179A.

[107] U.S. Pats. 1266955 and 1266956; *J.*, 1918, 543A.

[108] Ger. Pat. 306028; *J.*, 1918, 575A.

[109] U.S. Pats. 1274323 and 1274324; *J.*, 1918, 651A.

Paper Testing.

Systematic paper testing is being developed in America under Government auspices far more than in this country, and the organisation of research in this department makes a fair bid to rival that of Germany. The methods noted below all come from the same American laboratory and indicate that the subject is in charge of capable hands.

C. F. Sammet[110] has devised an apparatus for determining the translucency of paper by measuring the absorption of light transmitted through the paper and reflected back; by the difference in illumination between black and white backgrounds covered with the paper.

E. O. Reed[111] discusses the shortcomings of the previous methods for testing the absorbency of blotting paper, and shows that they do not sufficiently reproduce the conditions under which the paper is actually used. A new method has been worked out, and the details closely standardised; it is based on the measurement of the rate of absorption of 1 c.c. of standard ink dropped from a pipette on to the surface of the paper on a horizontal annular support.

Lastly, F. P. Veitch and E. O. Reed[112] have described the construction of an insulated room for the mechanical testing of paper under standard conditions of temperature and humidity. The ventilating air, passing over steam coils or brine pipes, is controlled by a thermostat and hygrostat situated inside the room.

[110] *J. Ind. Eng. Chem.*, 1917, **9**, 784; *J.*, 1917, 1004.
[111] *J. Ind. Eng. Chem.*, 1918, **10**, 44; *J.*, 1918, 85A.
[112] *J. Ind. Eng. Chem.*, 1918, **10**, 38; *J.*, 1918, 85A.

BLEACHING, DYEING, PRINTING, AND FINISHING.

By S. H. Higgins, M.Sc.,

Chemist, Bleachers' Association Ltd.

In selecting the papers for mention, as being of interest to those engaged in this branch of chemical industry, it must be admitted that there is a large field to cover, for the intelligent bleacher or dyer is interested in work on fats, proteins, cellulose, &c., and research work in biological chemistry may be of great interest to him, although it cannot be classed as belonging to this section of chemical industry. Overlapping is bound to arise. For instance, the constitution and properties of dyestuffs are of vital importance to the dyer as well as to the dyestuff manufacturer, and the production of colours on the fibre are really cases of dyestuff manufacture, although they are methods used in dyeing. If, therefore, a paper is of importance to those engaged in this branch of industry, this point is emphasised, in spite of the possibility of that paper belonging to another section.

The number of papers published shows a decrease, probably owing to the fact that the best brains have been engaged in other work. Notable papers have been given by W. Harrison[1] and S. J. Lewis[2] on the application of physics to textiles, and such papers as these, by inducing entirely new thoughts on these matters, are bound to lead to results of industrial importance, although it must be admitted that chemical investigations in this field apparently offer more chance of immediate returns. Leeds has of late become prominent in the application of physical science to the textile industry. A number of industrial concerns have taken up research and some have catered for the physical side of investigation. Few of the results obtained, however, are likely to see print, and this is not a pleasant factor to contemplate. Certainly, results of scientific interest only should be published without any indication of how they have been used in industry, for the publication of some results causes a worker to take more interest in scientific journals than he otherwise would.

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[1] *Proc. Roy. Soc.*, 1918, A, **94**, 460; *J.*, 1918, 460A.
[2] *J. Soc. Dyers and Col.*, 1918, **34**, 167; *J.*, 1918, 542A.

Almost everybody engaged in this branch of chemical industry is convinced that research is to be a necessary part of the industry, but great efforts will require to be made to keep up this enthusiasm. It must here be pointed out that it is a great mistake to say that the German dyeing industry is in advance of ours. On the other hand, just as this country is foremost in textile manufacture, so also is this lead kept as regards the subsidiary industries of bleaching, dyeing, printing, and finishing. But this position should not suffice. Now that we have the lead, it behoves us to keep it, and research will be one means to that end.

Some progress has been made towards the establishment of a Cotton Research Institute, to be devoted to research in connection with industries using the cotton fibre, and also to the education, particularly technical education, of those engaged in the industry. Preliminary steps have been taken by the Silk Association to form a Silk Research Association, and already researches have been instituted. Then we also hear that the Saxon Government has promised to form a Textile Research Institute. The Department of Scientific and Industrial Research is negotiating with the Irish linen manufacturers for the establishment of a Research Association, and this body has also made a grant to the Textile Institute to assist in the cost of their journal—that is, to ensure the abstracting of matter of interest to textile workers.

Of the actual research performed, a number of papers have been published by the Society of Dyers and Colourists and grants in aid have been made. The list of proposed investigations is long, but, owing to the international situation, difficulty has been experienced in getting suitable workers to carry out the investigations.[1]

At the present time a large amount of work is being done, all over the world, on the constituents of vegetable products, and this work will affect many industries. For instance, work on the constituents of textile fibres will have a marked influence on the textile industries and their subsidiary industries. Much work has already been done on the constituents of the cotton fibre, but the subject is a very large one. Perhaps the proposed Cotton Research Institute could not make a better start than with the investigation of this subject. Other vegetable fibres could also be investigated at the same time. Further, this Institute ought first to get the support of chemists and others engaged in the different branches of the industry. By discussions between chemists engaged in kindred industries mutual benefit would be derived and much duplication of labour avoided. Moreover, the work of the proposed Cotton Research Institute would be greatly assisted by the co-operation of the chemists mentioned, for these men, with a thorough knowledge of the chemical and other sides of their industries, would be of great use in organising this research work. Proper organisation would be of far more use than financial assistance from the Government, for the sooner industry learns that research pays for its own sake the better.

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[1] *J.*, 1918, 57R.

A recent report[4] states that the offer of £150 a year (as a pre-war standard) is not sufficient to entice good men into industry, but the present writer thinks that this initial remuneration, provided with good prospects and additional rewards for good results, will be sufficient to attract students to the branch of industry under consideration. At present there are a number of chemists of distinction engaged in the dyeing and allied industries, but the number of university graduates is not large. Probably most students were warned not to enter this branch of industry because the outlook was poor and the chances of promotion small. But the industry requires these men in order to progress.

It is not out of place here to mention the following remarks by B. Johnsen and R. W. Hovey:[5] "Cross and Bevan claim that the cellulose residues obtained from wood are not true celluloses of the same type as cotton cellulose, but that they are, in properties, true oxycelluloses, giving furfural as a typical reaction. It must, however, be remembered that the furfural reaction is by no means a characteristic reaction for oxycellulose, since, for instance, the typical oxycellulose obtained by treatment with calcium hypochlorite solution does not give the reaction. Moreover, these cellulose residues do not show the most typical oxycellulose reaction, namely the high reducing power (copper number)." Then M. Cunningham[6] states that the whole question of the structure of the cellulose complex remains open, and Cross and Bevan[7] throw doubt on the usually accepted furfuroid-pentosan relationship. The present writer also thinks that the celluloses should be re-grouped, or at least some definite distinction should be drawn between the groups suitable for plant physiologists and those suitable for chemists. With the advance in our knowledge of the constituents of fibres, these fibres should now be classed according to the nature of the cellulose they yield on treatment. For instance, cotton and flax fibres contain similar non-cellulose constituents, although the proportions of these constituents are quite different in the two cases, and the celluloses, which are isolated from these fibres by the bleaching process, are chemically indistinguishable. These fibres ought, therefore, to be classed in the same chemical group, in spite of the fact that one is a seed hair and the other a bast fibre.[8] The use of such terms as pure, pecto- or adipo-cellulose are not required to distinguish these fibres. It is true that flax contains a small quantity of woody matter, but this is of little importance in the numerous operations through which the fibre is put, and the statement that flax cellulose is more easily hydrolysed than cotton cellulose is not supported by the observation of the present writer that forty hours' boiling of scoured linen yarns, under pressure with alkalis, had no apparent weakening effect. If, after isolating the cellulose from a fibre, this cellulose is found to be different chemically from the cellulose of cotton, there is justification for putting it in another chemical group; but if it is not chemically different then it should be grouped with cotton. Grouping in this manner will tend to simplify matters and enable some order to be introduced into the present chaos of cellulose chemistry. In the case of another carbohydrate, viz., sugar, existing in plants, sucrose is given that designation, whether it be isolated from the sugar-cane, beet, or the maple tree. If, however, the sugar isolated is not identical with sucrose, it is put in another class. It is true that in the case of sugar, which is crystallisable, the grouping is simpler than in the case of different forms of cellulose, but the case of starch in the vegetable kingdom forms a better analogy. It is known that all forms of starch occurring in the vegetable kingdom are not precisely the same,[9] and all samples, like the celluloses, yield a small amount of ash on incineration, showing that they are complex substances; yet it must be admitted that collecting all the forms of starch together and calling them "starch" has simplified matters and assisted progress in operations in which starch takes part.

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[4] Report of the Committee appointed by the Prime Minister to enquire into the position of natural science in the educational system of Great Britain, 1918 p. 73.

[5] *J.*, 1918, 136T.

[6] *Chem. Soc. Trans.*, 1918, 113, 173: *J.*, 1918, 236A.

[7] *Ibid.*, 182–187; *J.*, 1918, 236A.

BLEACHING.

Further work has been done on the discoloration of cotton and linen goods during storage. This subject was referred to at length in Annual

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[8] It has been shown (E. Heuser and A. Haug, *Z. angew. Chem.*, 1918, **31**, 166, 172; *J.*, 1918, 650A) that the cellulose separated from straw is indistinguishable from cotton cellulose.

[9] See A. R. Ling, *Annual Reports*, 1917, 406.

Report, 1917, and it was pointed out that proper scouring and bleaching was the only method of preventing this fault. The present writer remembers a case of cotton piece-goods being bleached by wetting out, saturating with bleaching powder solution, allowing to lie for some time, washing, souring, and again washing. Goods bleached in this way were a fair white, but would probably deteriorate on storage. They would certainly lose their whiteness on steaming, because the non-cellulose constituents of the cloth had merely been oxidised on the fibre and only partially removed. The fats and waxes are not destroyed by the hypochlorite, and on steaming they melt, thus causing the cloth to become darker in colour. Linen which had been given a three-quarter bleach, was found to turn yellow on steaming, and the only way to prevent this change of colour was by bringing the bleach from a three-quarter to a full white.[10] M. Freiberger[11] concludes that fats play no appreciable part in the yellowing of goods during steaming, whereas "gums" cause yellowing during both dry heating and steaming. He states that the yellowing is due to β-oxycellulose. He again emphasises the advantage of using warm sodium hypochlorite containing an excess of soda,[12] since goods chemiced in the ordinary way show a much stronger discoloration. The author would require to state more fully what he means by the "gums" of cotton, and perhaps some further information might be desired concerning what he designates as β-oxycellulose.

As regards the tendering of bleaching vegetable yarns during storage, this fault has been shown by Higgins (*loc. cit.*) to be due to mineral acids which have not been completely washed out of the goods. It was shown that acid was very difficult to wash out of vegetable fibres. In the "creaming" of linen yarns there is a great danger of leaving acid in the yarns after the last washing process, and this acid might subsequently cause trouble. "Creaming" could be produced with less risk by using sodium hypochlorite and dispensing with the acid treatment altogether. Both as regards linen and cotton the writer was unable to agree with Cross, Bevan, and Briggs[13] that chloramines have important functions in bleaching operations. In fact, his experiments pointed to the conclusion that chloramines were of no interest to the bleacher. C. F. Cross replied by letter to the above-mentioned conclusions, and later J. F. Briggs took up the subject. Readers are referred to those letters and also to two by Higgins in the same journal.[14] The present writer cannot be expected to give an impartial view of this controversy; but perhaps it is sufficient to say that his further work has shown that, after the scouring operations generally used in the bleaching of cotton and linen goods, these fibres contain practically no proteins. Alkalis are excellent solvents for proteins, and in the long boiling with alkalis in commercial bleaching operations the proteins are effectively removed. As a consequence, when these fibres enter the bleaching powder solution for the first time they contain practically no proteins. The possibility of forming chloramines is therefore small, except of course from any proteins present in the water used in making up the hypochlorite baths. In this connection it is interesting to note the claim[15] that proteins on hydrolysis with caustic alkalis yield products which, on treating with calcium or magnesium hydroxide, give substances useful as detergents and employed in dyeing and printing.

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[10] S. H. Higgins, *J. Soc. Dyers and Col.*, **1918, 34, 35; *J.*, 1918, 265A.**

[11] *Färber-Zeit.*, **1917, 28, 221, 235, 249; *J.*, 1918, 468A.**

[12] *Annual Reports*, **1917, 163.**

[13] *J.*, **1908, 260.**

The connection between bleaching solutions and antiseptics used in surgery has been pointed out,[16] since all the hypochlorites which have been used in different forms during the war had previously been used as bleaching agents, thus strikingly showing the relation which exists between different branches of experimental science. Sodium hypochlorite produced by electrolysing a solution of common salt contains a large amount of unaltered salt; by adding boric acid to this solution an ideal antiseptic for surgical purposes would be produced.

Regarding the properties of hypochlorites the remarks of R. L. Taylor[17] on the effect of exposure to light are of interest to bleachers. He had previously[18] suggested exposing hypochlorite solutions to air before use in order to increase their bleaching efficiency, but Higgins[19] showed that by the time the hypochlorites had increased in bleaching efficiency they had lost a large proportion of their available chlorine. Taylor now suggests that hypochlorites be preserved from the action of light.[20] T. Rettie, J. L. Smith, and J. Ritchie[21] suggest mixing freshly ignited quicklime with bleaching powder intended for export to hot countries, since in this way the loss of available chlorine is largely avoided and the formation of calcium chlorate inhibited. It is known that the addition of hydroxides to hypochlorites increases their stability, and, in the case of bleaching powder, this fact is also expected to hold,

[14] *J. Soc. Dyers and Col.*, 1918, **34**, 76, 127, 176, 302.

[15] C. Bennert, Ger. Pat. 304003; *J.*, 1918, 412A.

[16] S. H. Higgins, *J. Soc. Dyers and Col.*, 1918, **33**, 189.

[17] *J. Soc. Dyers and Col.*, 1917, **33**, 246; *J.*, 1918, 86A.

[18] *Chem. Soc. Trans.*, 1910, **97**, 2541.

[19] *Ibid.*, 1911, **99**, 858.

[20] See also White, *J.*, 1903, 132.

[21] *J.*, 1918, 311T.

since the powder is hygroscopic; but it must also be remembered that the addition of hydroxides, while increasing the stability, decreases the bleaching properties of hypochlorites, and also, from what has been stated above, the addition decreases the antiseptic properties. The lime which is added to the bleaching powder could not be separated when it has served its purpose, and the solution produced would have weaker bleaching and antiseptic properties because of the presence of the lime. In connection with hypochlorites used for bleaching, the claim[22] for producing a dilute bleaching liquor by passing chlorine into sodium carbonate solution, then adding more sodium carbonate, is of interest, and also[23] the production of a high strength bleach by the reaction of steam and chlorine at about 100° C. to give hydrochloric acid and hypochlorous acid, the former being removed by condensation and the latter by absorption in caustic alkali.

A process which has recently been discussed and tried by some bleachers[24] depends on the stimulating effect produced by adding sodium bicarbonate to bleaching powder solution. This effect has been described by Higgins[25] and used by H. D. Dakin in the preparation of antiseptics. In the particular process under consideration the cloth is impregnated with a solution of sodium bicarbonate and then run into the bleaching powder solution. The result is an active bleaching agent and the production of some calcium carbonate. This calcium carbonate has to be subsequently removed from the material by treatment with hydrochloric acid. Now suppose the cloth be treated with weak hydrochloric acid instead of bicarbonate when entering the bleaching powder solution. The result will be exactly the same, with the additional advantage that no insoluble calcium carbonate will be produced. This is an old method of procedure among bleachers, and, carefully performed, it is a far better method than the more recently proposed one.

A. Poulsen[26] bleaches loose fibres and other materials by boiling in a mixture of sodium carbonate and bicarbonate and then treating with sodium hypochlorite solution, while H. R. Anders[27] uses lime for the boiling, and lime and a "substance carrying oxygen" for the bleaching.

The injurious effects of perborate soaps and similar peroxide bleaching agents is pointed out by P. Heermann.[28] Metallic salts, *e.g.*, of copper and iron, stimulate this destructive action, and these salts are often present in small quantities in stains on linen and cotton goods.[29] In reply to attacks on his paper, Heermann[30] supports his previous statement and contends that washing powders containing available oxygen will produce in some cases local destruction and perforation of fabrics. This fact had previously been proved.[31]

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[22] Deutsch Solvay-Werke Act.-Ges., Ger. Pat. 306193; *J.*, 1918, 581A.

[23] K. P. McElroy, U.S. Pat. 1261572; *J.*, 1918, 415A.

[24] J. E. Macilwaine, Eng. Pats. 28911 (1913) and 6317 (1914); *J.*, 1915, 75.

[25] *J. Soc. Dyers and Col.*, 1912, 28, 30.

[26] Eng. Pat. 104048; *J.*, 1917, 383; 1918, 179A.

[27] U.S. Pat. 1251614; *J.*, 1918, 121A.

[28] *Chem.-Zeit.*, 1918, 42, 85; *J.*, 1918, 238A.

S. J. Pentecost[32] calls attention to the presence of iron in some samples of nitre cake and the possibility of it causing trouble if used for bleaching. Sodium silicate has been found to have an injurious action on cotton textiles in the presence of soft water; after washing with the silicate the goods are dull and chalky. The use of hard water caused the textile fabrics to have a higher strength after washing with soap, soda, &c.[33]

The permanganate bleach for silk is stated[34] to be preferable to that using peroxide, nitrite, or *aqua regia,* but care should be taken to avoid the presence of alkalis in the bath. A small amount of sulphuric acid is added. A better colour could not be obtained by repeated bleaching, for with many treatments a falling off in colour was noticed, the silk becoming brown and losing in weight and tensile strength.

A paper[35] on the valuation of lime is of interest to bleachers.

DYEING.

A development of the production of natural indigo is reported,[36] the result being a paste which has been found superior to synthetic indigo paste for heavy shades. It cannot be used for light shades, however, because of impurities. E. R. Watson[37] records a considerable loss of indican during the air drying of the indigo leaf and suggests the immediate steeping of the leaves.

The nature of the mordanting process is discussed by A. B. Clark,[38] a relation being shown to exist between the mordanting power of a metal and its position in the periodic table. The mordanting action of ferro- and ferricyanides is dealt with. Of the different examples of dyeing with mordants which have been described we have: The extract of the leaves of *Acer ginnala* gives black and grey shades on an iron mordant, khaki shades [39] on a chrome mordant, and extract of wattle, which probably contains tannin in some form, produces shades of brown, fawn, grey, and drab on wool and cotton.[40] As mentioned in Annual Report, 1917, a diligent search has been made for natural colouring matters in order to substitute the dear and, in some cases, unprocurable artificial varieties. O. Diehl [41] describes the production of a fast black on an iron mordant by means of a mixture of alizarin and dinitroresorcinol, and F. C. Schmidt,[42] for the dyeing of logwood black on silk, protects methods of reducing the number of tin phosphate baths, and for obviating the usual treatment with tannic acid and with an aniline dyestuff for the purpose of topping. Further, the substitution of sodium silicate for soap in the dyeing bath is claimed to give a higher loading. A shade similar to naphthylamine claret, and not having the objections of that dyestuff, is said to be produced by dyeing with a mixture of alizarin and alizarin cyanin on an aluminium mordant.[43]

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[29] See also J. F. Briggs, *J.*, 1916, 80; S. H. Higgins, *J.*, 1911, 188.

[30] *Chem.-Zeit.*, 1918, **42**, 337, 342; *J.*, 1918, 576A.

[31] S. H. Higgins, *J. Soc. Dyers and Col.*, 1912, **28**, 30.

[32] *J.*, 1918, 169R.

[33] A. Grün and J. Jungmann, *Seifenfab.*, 1917, **37**, 507, 529, 553, 579, 603; *J.*, 1918, 411A.

[34] E. Ristenpart, *Färber-Zeit.*, 1918, **29**, 37; *J.*, 1918, 410A.

[35] R. K. Meade, *J. Ind. Eng. Chem.*, 1918, **10**, 214; *J.*, 1918, 239A.

[36] *J.*, 1918, 261R.

[37] *J.*, 1918, 81T.

[38] *J. Phys. Chem.*, 1917, **21**, 776; *J.*, 1918, 86A.

There is a decrease in the number of examples of dyestuffs developed on the fibre, only one method having been protected. Dyestuffs of a reddish blue shade are produced on the fibre by diazotising in the usual way, then developing with an N-alkyl derivative of chloro-*m*-phenylenediamine.[44]

In the production of aniline black, E. Bechtel [45] states that a mixture of hydrochloric acid and nitric acid may be used with advantage in place of the former acid, and sodium ferrocyanide may replace the potassium salt. Since ferrocyanide, aniline oil, and acids give a blue on vegetable fibres, there is a tendency to a blueish black. The Calico Printers' Association and E. A. Fourneaux have protected a further method of producing aniline black,[46] and a previously described process [47] has been modified in that the use of aluminium chloride has been dispensed with and the proportion of *p*-phenylenediamine reduced. The presence of formic acid is necessary, but it may be used along with other acids.[48] Further, the use of boric acid, either alone or with phosphoric acid, is protected [49] in order to prevent the loss of aniline during careless drying. In a further patent [50] various stipulations as to the amounts of the ingredients are made and the order in which the ingredients are used specified.

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[39] *J. Chem. Ind., Tokyo,* 1918, **21,** 211; *J.,* 1918, 462A.

[40] *J. Roy. Soc. Arts,* Mar. 15, 1918.

[41] *Färber-Zeit.,* 1917, **28,** 233; *J.,* 1918, 411A.

[42] Ger. Pats. 305275 and 305770; *J.,* 1918, 464A.

[43] O. Diehl, *Färber-Zeit.,* 1917, **28,** 212; *J.,* 1918, 411A.

[44] Act.-Ges. f. Anilinfabrikation, Ger. Pat. 303409; *J.,* 1918, 412A.

[45] *Färber-Zeit.,* 1917, **28,** 300; *J.,* 1918, 462A.

[46] Eng. Pat. 115278; *J.,* 1918, 367A.

[47] Eng. Pat. 7345 (1908); *J.,* 1909, 701.

The addition of fat-splitting agents, such as Twitchell's reagent, to the dye-bath, in order to produce emulsification, has been protected.[51] In hydrosulphite vats a homogeneous emulsion is produced on stirring.

The theory of dyeing has been discussed by members of the Society of Dyers and Colourists.[52] This subject was referred to at some length in Annual Report, 1917, and by P. E. King.[53] Besides the old chemical and mechanical theories of dyeing there are many explanations of dyeing phenomena which lie between these theories; some observations, such as the dyeing of vegetable fibres by substantive cotton dyestuffs, are not regarded by any group of chemists as being due to chemical reactions. It must be admitted that in this realm of speculation, progress will largely depend in the advance of our knowledge of physical chemistry, on the development of the theories of ionisation and of the colloidal state. As pointed out in Annual Report, 1917, the attraction of moisture by fibres is a process, concerning the mechanism of which explanations are very varied, but there seems to be a connection between this absorption and adsorption during dyeing processes. W. Harrison [54] states that the electrical theory of dyeing provides explanations where the chemical theory fails, although it is not opposed to the latter theory. T. R. Briggs, H. S. Bennett, and H. L. Pierson [55] describe an electrical endosmometer, and discuss their observations on solutions of acid and basic dyestuffs with reference to the adsorption theory of dyeing. In studying the distribution of basic dyestuffs between isobutyl alcohol and water it has been found [56] that the presence of sodium salts of different acids affords a series in which the anions are arranged in the same order as in the lyotropic series. In the case of the adsorption of dyestuffs by blood charcoal this lyotropic influence was also noticed, and the authors suggest that this line of inquiry should be productive of elucidation of the dyeing process. Two papers on the dyeing process have been published by R. Haller. In one [57] he points out that jellies formed by certain substantive cotton dyestuffs with water are similar to soap jellies, and the formation of the jellies seems to be dependent on the presence of small quantities of an electrolyte in the dyestuffs. The action of these electrolytes cannot be explained, but it is evident that they play an important part in the technical application of these dyestuffs. In a second paper [58] he states that the adsorption compounds of dyestuffs, with a crystalline substance such as barium sulphate and with a colloidal substance such as cotton, behave as mechanical mixtures rather than as chemical compounds, the difference in the compounds being entirely due to the varied physical characteristics of the adsorbents. The mixture hypothesis is supported by the behaviour with solvents, the nature of the adsorption spectra of the solutions, and the determination of the melting-points. In the case of mordants, chemical compounds are probably formed with dyestuffs, these compounds subsequently forming adsorption compounds with the fibre during the process of dyeing.

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[48] Eng. Pat. 113484; *J.*, 1918, 204A.

[49] Eng. Pat. 116562; *J.*, 1918, 463A.

[50] Eng. Pat. 117987; *J.*, 1918, 576A.

[51] S. Aschkenasi, Ger. Pat. 303121; *J.*, 1918, 367A.

[52] *J.*, 1918, 111R.

[53] British Association: First Report on Colloid Chemistry and its Industrial Applications, 1917.

[54] *J.*, 1918, 111R.

[55] *J. Phys. Chem.*, 1918, **22**, 256; *J.*, 1918, 380A.

[56] H. R. Kruyt and J. E. M. van der Made, *Proc. k. Akad. Wetensch. Amsterdam*, 1918, 20, 636; *J.*, 1918, 238A.

An exchange of opinions has taken place between W. Harrison and M. Fort over the behaviour of wool towards acids and solutions of dyestuffs. Harrison [59] found that wool which had been treated with acid gave up all this acid to boiling water on repeated extraction, and that the extracted wool had no greater affinity for dyestuffs than the untreated wool.[60] He concluded that the dyeing of wool with acid dyestuffs is a colloidal chemical phenomenon. Fort [61] replied that on treating wool with acid, the acid cannot be entirely washed out of the wool. He points to the practical value of the theory of the acid-wool compound as opposed to theories based on little understood electrical phenomena, and states that Harrison's results do not explain the decomposition of neutral salts by wool. The behaviour of wool in dyeing operations, he states, is due to its protein contents. It has often been pointed out that wool holds acid very tenaciously, and the present writer remembers washing a sample, which had been treated with acid, for a long period with distilled water; on that occasion it was found that the wool still retained a slight amount of acid. Recently much advance has been made in determining the nature of the constituents of textile fibres, and also much headway has to be recorded as regards our knowledge of proteins. Theories of dyeing must make room for this knowledge and assimilate the fact that proteins, which are contained in raw vegetable fibres to a small extent and in animal fibres to a larger extent, have sometimes basic and sometimes acid properties, according to the nature of the substances presented to them. Fort's remark that belief in the chemical theory of dyeing is helpful in practical matters cannot altogether be regarded as evidence. The present writer has always been as convinced of the mechanical theory, and in dyeing operations he always has upheld this theory and indeed used it as a guide. It is possible that with those using vegetable fibres the mechanical theory of dyeing is taken for granted, while in other centres, namely, woollen districts, the chemical theory is supported. Of this contention we have a notable example in the late Walter Crum.

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[57] *Kolloid Zeits.*, 1918, **22**, 49; *J.*, 1918, 365A.

[58] *Kolloid Zeits.*, 1918, **22**, 113; *J.*, 1918, 411A.

[59] *J. Soc. Dyers and Col.*, 1918, **34**, 57; *J.*, 1918, 238A.

[60] Compare M. Fort and L. L. Lloyd, *J.*, 1914, 133, and M. Fort, *J.*, 1913, 907.

[61] *J. Soc. Dyers and Col.*, 1918, **34**, 124; *J.*, 1918, 410A.

As regards the fastness of dyestuffs to light, the efficacy of a layer of oil or wax in excluding the unfavourable influence of moisture and thus increasing the fastness has been mentioned.[62] The fading of dyestuffs may be prevented by the dislocation of the original equilibrium between the oxygen in solution and the ions of the water (the perhydroxyl ions), by preventing or impeding the reactions between the dyestuff and the perhydroxyl ions and by the transformation of the dyestuff peroxide into more stable compounds. A. Robson [63] describes a method of standardising the fastness of dyestuffs to light by the measurement of the quantity of actinic light required to produce a visible change in the tone or depth of the test sample. This is assisted by noting the number of consecutively exposed standard strips of a quickly fading colour, which are completely bleached under the same conditions. Objections to the method are admitted.

The number of dyeing machines which have been described is few, and apparently no distinctive advance has been made. A machine for dyeing yarn on the pack system [64] arranges that the flow of dyestuff solution takes place by force from the side walls of the machine and along the threads to be dyed placed horizontally in the machine and approximately in the direction of the flow.

That the different processes of dyeing have an effect on the combustibility of the finished material has been pointed out by G. E. Holden.[65] The ultimate destination of the goods and the burning test should receive consideration before selecting processes of dyeing. W. Thomson [66] called attention to the fact that black dyed velveteens, containing iron, burned until only the ash remained, whereas other velveteens, dyed with different dyestuffs but containing no appreciable amount of iron, gradually became extinguished.

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[62] K. Gebhard, *J. Soc. Dyers and Col.*, 1918, 34, 74; *J.*, 1918, 265A.

[63] *J. Soc. Dyers and Col.*, 1918, 34, 185; *J.*, 1918, 619A.

[64] J. Annicq, Eng. Pat. 113575; *J.*, 1918, 204A.

[65] *J. Soc. Dyers and Col.*, 1918, 34, 7; *J.*, 1918, 121A.

[66] *Ibid.*

MERCERISING.

The strength and elongation of mercerised yarns has been shown [67] to depend on the thorough removal of the caustic soda after mercerising, on the amount of stretching to which the yarns are subjected in the mercerising machine, and on the moisture contained in the yarn before mercerisation. A number of effects produced on cotton fabrics by alternately exposing them to caustic soda and sulphuric acid solutions were described in Annual Report, 1917, and a further variation of the treatments has been protected. Heberlein & Co. [68] produce transparent effects on cotton goods by treating with caustic alkali of a density above 20° B. at temperatures below 0° C. The transparency is increased by subjecting the treated fabric to sulphuric acid of about 50·5° B. In the U.S. Patent [69] the conditions mentioned are treatment with caustic alkali solution of at least 15° B., washing, and then treating with sulphuric acid of at least 50·5° B., both treatments being carried out at a temperature below 0° C.

As regards the theory of the mercerising action, W. Harrison [70] regards the shrinkage which takes place during mercerisation as being due to the balancing of the internal stresses of the fibres. He studied this action by using polarised light (see p. 161). Regarding the twists in the natural fibres, W. L. Balls [71] points out that when the cotton plant is thirty-three days old it is easy to distinguish simple pits in the cell-walls of the fibres; these pits are common in many kinds of vegetable cell-wall and are not in any way peculiar to cotton. Given such pits, the fibre must twist when it dries unless the wall has been thickened so much as to obliterate the central cavity almost entirely. Twisting may be left or right; the direction appears to be accidental. Further, he states that lustre is probably almost synonymous with twist; if all the hairs in a sample are well and evenly twisted, there will be an infinite number of convex surfaces, each reflecting a spot of light. In addition to this there is diffraction of light which can be seen by holding a well-twisted fibre against a dull background with a good north light well overhead. It seems more than probable that the causes of lustre changes lie behind the cuticle, because the cuticle is one of the last plant tissues to be affected by ill-treatment. To the present writer these remarks offer a strong support to the theory of Huebner and Pope[72] as to the increase of lustre by mercerisation. Discussing the strength of yarns, Balls states that the strength, within limits, follows the amount of twist which is put into it, even the variations in the strength of yarn after mercerising being accounted for in this way.

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[67] T. Nakata, *J. Chem. Ind. Tokyo*, 1917, **20**, 1224; *J.*, 1918, 203A.

[68] Eng. Pat. 108671; *J.*, 1918, 297A.

[69] U.S. Pat. 1265082; *J.*, 1918, 461A.

[70] *Proc. Roy. Soc.*, 1918, A, **94**, 460; *J.*, 1918, 460A.

[71] "*The Development and Properties of Raw Cotton.*" A. & C. Black, Ltd., London.

The causticising of soda liquors has been fully discussed,[73] many systems being described, and the saving in space produced by using filter presses emphasised.

PRINTING.

In this branch of the industry only two papers call for comment. The fixation of dyestuffs during printing is brought about[74] by mixing with the dyestuff a substance containing a protein and a substance which yields formaldehyde at the temperature of the printing machine. The formaldehyde reacts with the protein. The Calico Printers' Association and F. Ashton[75] produce chromium mordants on vegetable fibres by immersing in a chromium salt solution and in caustic soda of strength not less than 20° Tw.

FINISHING.

As regards cotton sizing, R. H. Pickard[76] points out the empiricism of the process and the need for research. The investigation of this process, however, is difficult because of such intangible characteristics as the feel and appearance of cloth, which do not allow of definite measurement. The same remarks apply to the finishing of dyed and bleached goods; experience is still the only factor in this branch of the industry. A method of finishing fabrics by exposing them in the open width to a variety of operations, including brushing, exposure to steam, calendaring, and stretching has been protected.[77] W.

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[72] *J.*, 1904, **23**, 404.

[73] M. L. Griffin, W. H. Howell, jun., and G. K. Spence, *Met. and Chem. Eng.*, 1917, **17**, 599; *J.*, 1918, 28A.

[74] C. Jäger G. m. b. H. and R. W. Carl, Eng. Pat. 116109; *J.*, 1918, 464A.

[75] Eng. Pat. 117715; *J.*, 1918, 576A.

[76] *J.*, 1918, 26R.

[77] Columbia Conditioning Co., U.S. Pat. 1270153; *J.*, 1918, 577A.

Harrison[78] states that double refraction in textile fibres is due to internal stresses which may be increased by compressing the fibres. When the pressure is released, the fibres do not revert to their original form nor lose their increased double refractive powers until immersed in cold water; but cold water is not capable of influencing the natural internal stresses of the fibres. At high temperatures, water renders fibres plastic, and deformation produced by compression does not cause internal stresses. These observations are of interest in studying the calendaring and other finishing process. Such investigations may succeed in infusing some scientific information into the empiricism of finishing. M. Fort[79] records a case of mechanical powdering of the cotton fibre during the beetling process. A deposit resembling lumps of starch was obtained which was easily crushed to a smooth powder. The product still had the properties of cellulose.

In the weighting of silk, the weighting liquors—phosphate, and stannic chloride—are alternately forced through the fabric rolled on a metal drum. The drum is then removed to a drying machine and the fabric is dried by centrifugal action. The treatment is repeated until the desired loading is obtained.[80]

For the treatment of waste liquors from textile and dye works, the use of chlorides or sulphates of alkaline earths and then highly plastic clay has been protected.[81]

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[78] *Proc. Roy. Soc.*, 1918, A, **94**, 460; *J.*, 1918, 460A.

[79] *J. Soc. Dyers and Col.*, 1918, **34**, 9; *J.*, 1918, 121A.

[80] F. J. B. Knibiehler and A. Fankhauser, U.S. Pat. 1259526; *J.*, 1918, 297A.

[81] C. Gunkel, Ger. Pat. 304040; *J.*, 1918, 484A.

REPORTS
OF THE
PROGRESS OF APPLIED CHEMISTRY.

PLANT AND MACHINERY.

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Owing to the armistice and the consequent closing down of several of the factories engaged for the war effort in industrial chemistry, some of the developments in plant and machinery are becoming known. Such developments always confirm the importance of the scientific study of the problem for solution and the value of more than one factory or set of brains being engaged on the same problem at the same time.

There are few improvements to record in materials of construction. Acid-resisting iron castings are certainly more reliable in use, and more "feeling" for the material is shown in the designs. More uniformity in thickness, avoidance of sharp corners, corrugation of large flat surfaces, &c., are points to which more attention is given.

An example occurs in trays used for the concentration of sulphuric acid in cascade plants. Since boiling in these plants involves projection of liquid and the breaking of joints between the gas and fire flues in addition to other consequent troubles, the best work is usually done with such plants when the maximum evaporation is obtained without boiling. The best vessel is therefore one which provides the maximum area of surface for evaporation with the minimum volume of liquid. An oblong flat tray provides these conditions, but is difficult to cast in acid-resisting iron and is liable to breakage in work through internal stresses. S. J. Tungay and G. B. Haughton[1] get rid of this difficulty by corrugating the surfaces which were formerly flat.

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[1] Eng. Pat. 114072; *J.*, 1918, 266A.

The addition of 2% of nickel to the usual alloy of iron with 15% of silicon improves the material, no doubt through its effect in preventing segregation.[1] An Italian maker claims that his material resists hydrochloric acid, but this remains to be proved. Another acid-resisting metal, ferro-boron (15% B, 5% Si, and 3% each of Al and Mn) has been found to be a failure in practice. The original French material, *métallure*, is still one of the most reliable of these acid-resisting irons. Borchers' metal (2 parts Ni, 1 part Cr, with 0·5% Ag and 1·3% Mn), although an excellent acid-resisting metal, is obviously too costly to supersede iron-silicon alloy for commercial work.[2] A copper-nickel alloy resisting sulphuric acid has been patented by F. Milliken.[3] It contains 60–70% Cu, 6–9% Ni, 4–6% Fe, 12–16% Zn, and 2–3% Pb. R. Irmann states [4] that a copper-nickel-tungsten-iron alloy (Cu 46·65, W 3·9, Fe 1·87%) is highly resistant to hot sulphuric acid and is at the same time extremely strong and ductile.

More attention is now being paid to the quality of ordinary chemical cast iron, and better material is now easily obtainable. The irregular quality of the metal, which can hardly be avoided by the ordinary method of melting in a cupola, is the most serious fault. Crucible or open-hearth melting of cast iron would no doubt give the chemical engineer that dense, uniform, and strong metal which he wants. The addition of a small percentage of nickel would still further improve it. It is likely that the cost of such cast metal would not be seriously higher, while it is certain that the economic result would be most satisfactory.

The centrifugal method of casting straight iron pipes, which is now in successful operation, will probably displace the ordinary method of casting pipes in course of time, on account of the increase in density, strength, and anti-corrosive qualities of the metal. Such pipes are cast in a horizontal rotating open mould in a few seconds, a suitable core being provided where the socket is formed. Heat treatment is necessary to make machining readily possible and is the subject of a patent.[5] The casting of a "bead" on pipes is not easy by this method, while it is fairly certain that it is not good practice, owing to the absence of provision for expansion and contraction.

English chemical stoneware is giving excellent service, and it is certain that the continental product will not compete in future on a quality basis. "Ceratherm," a special variety of high strength and thermal conductivity with a very low coefficient of expansion, has been very successful under the most trying conditions.

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[2] C. Matignon, *Comptes rend.*, 1918, **166**, 815; *J.*, 1918, 375A.

[3] Eng. Pat. 118825; *J.*, 1918, 660A.

[4] *Metall u. Erz*, 1917, **14**, 21, 37; *Engineering*, 1917, **104**, 610; *J.*, 1917, 928.

[5] D. S. de Lavaud, U.S. Pat. 1280418; *J.*, 1918, 771A.

H. Stegmeyer[6] claims that a composition of porcelain dust and silicate of soda, formed, dried, and then heated under pressure in an atmosphere of carbon dioxide, will stand concentrated sulphuric acid better than ordinary chemical stoneware.

A valuable series of suggestions for the standardisation of chemical stoneware plant has been made by H. Nielsen and J. R. Garrow.[7] These suggestions are excellent and come at an opportune time. Unfortunately, the strength of the material, on account of the method of manufacture, is not proportional to its thickness. The authors recognise this by suggesting 2¼ inches as the limit of thickness. Any method of calculating the strength of stoneware plant must be open to adverse criticism, and the authors' method of assuming the material to be homogeneous, with a tensile strength of 600 lb. per sq. inch, can only be considered a temporary expedient. The actual breaking strength of a sample piece of plant should be determined. The authors adopt a factor of safety of 2 and suggest a test pressure of twice the pressure to be adopted in use. For pipe connections to pressure vessels they condemn pipe-necks and suggest thick bosses of square form in which are ground standard pipes of standard taper. Two longitudinal holes receive bolts carrying eye-bolts to hold the iron armature of the pipe flange, and so prevent the ground-in pipe from being blown off.

Alternative designs will occur to every chemical engineer who uses stoneware, and it is likely that the standards proposed by the authors will be modified before being adopted by manufacturers in general. For liquor pipes the joint may be made over a much smaller area than that indicated, with the advantage that less pressure is needed to make the joint, and incidentally consequent troubles are avoided. In many cases it is desirable to have these joints made of the "ball-and-socket" type. Such joints are just as easy to grind as flat joints, and in high-pressure work are more reliable, since they inflict on the pipe no more pressure than that required to make the joint. A "dead" parallel pair of faces on the last joint made is very uncommon in general work using flat joints, and a bending moment is often put on the pipe by the last joint. Two ball-and-socket joints avoid any trouble from this cause. Packing material that flows is generally superior to asbestos board for jointing, and soft lead or ribbon lead is most satisfactory under iron armatures to prevent local stress on the stoneware. The paper is full of valuable suggestions, and a set of tables of dimensions ought to make it possible for manufacturers to get into line.

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[6] Ger. Pat. 302834; *J.*, 1918, 335A.

[7] *Chem. Trade J.*, 1918, 62, 157, 179, 235; *J.*, 1918, 57A, 207A.

Several new designs of tower-filling material have appeared, but it is unlikely that any is more efficient than the simple ball or the Lunge plate. In most of these designs, besides the provision of a large effective surface, the object of the inventor has been to change the direction of flow of the gas as often as possible. On account of the very low velocity of the gases in an ordinary tower scrubber, it is probable that this notion in design is an inefficient one, but that to make many changes in area of the channels of flow, so that variation in velocity occurs with concomitant changes of pressure, is the most efficient principle of design. For this reason ball packing is very efficient, while the more recent designs of "cell filling," where this principle is most in evidence, are most satisfactory. On the other hand, the great defect of "ball filling," viz. lateral pressure on the sides of the tower, is avoided in the best types of cell.

A simple improvement in the design of Cellarius condensers is worth mentioning. The gas inlet and outlet sockets are placed out of centre so that the distance between sockets of adjacent condensers is reduced. A distinct and useful reduction of cost is thus obtained.

Brickwork construction for large chemical tanks, towers, concentrators, &c., with little or no external metal support or protection, is becoming quite reliable. Several suggestions for improving the cement used have been made. C. C. Meigs[8] adds an acid salt such as calcium phosphate, and in another patent[9] adds a chloride, claiming that it increases the hardness and density of the cement. Chance and Hunt, Ltd., A. E. Holley, and H. W. Webb[10] add 1·5% of lead carbonate or basic carbonate to make such cement quick-setting.

The use of wood in chemical engineering work calls for some consideration, especially as it is being displaced by steel, ferro-concrete, &c., in several types of plant. The value of different woods for acid tanks has been investigated by A. W. Schorger.[11] No wood will withstand nitric or sulphuric acid of any strength for any length of time, but such woods as cypress, pine, and sequoia resist weak hydrochloric acid up to 5% strength well. Red cypress (*Taxodium distichum*) is a wood rarely used in England by chemical engineers, for whose work it is particularly adapted. Californian red wood or sequoia is less rare, but its good properties are not so well known. On account of its very open structure and lightness it can be readily impregnated without elaborate apparatus, and is then of the greatest value in chemical work. Both timbers are very free from knots, do not warp or twist, and in addition can be had in large sizes. They are free from taint, odour, or taste, and are more valuable on that account for the pharmaceutical and food industries.

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[8] U.S. Pat. 1245608; *J.*, 1918, 31A.

[9] U.S. Pat. 1252013; *J.*, 1918, 125A.

[10] Eng. Pat. 119966; *J.*, 1918, 768A.

[11] *J.*, 1918, 397A.

The protection of wood by the use of paraffin and pitch is well known. An impregnating material consisting of petroleum residues and common rosin dissolved in petrol has been patented by W. V. Lander.[12] Maple soaked in paraffin is often recommended instead of teak for the plates of filter presses. In this connection a new varnish called "duroprene" (United Alkali Co., Ltd.) offers great advantages for all kinds of protective work. As usually sold, it consists of 15% of chlorinised rubber dissolved in benzene, and can be applied to any dry surface to protect it from acid or alkali corrosion. The varnish is extremely mobile and will penetrate the surface of the most impervious materials. The elastic film formed is most tenacious and impervious to gas diffusion. In the interests of cleanliness in the laboratory it should be used for benches, wooden and metal apparatus. For storage bins, chemical tanks, carboy boxes, filter-press plates, patterns for moulding, &c., it has great value, while for proofing fabrics, conveyor belts, machine belts, tarpaulins, &c., its advantages are obvious. By the addition of pigment it can be converted into an equally useful paint.

The introduction of ball bearings is one of many indications that the character of the engineering in chemical works is improving. Several makers are providing standard designs of stirring gear which are self-contained and can be mounted readily on any vessels with the minimum of trouble and expense. These stirring gears are usually provided with ball bearings.

The housings of ball bearings are always provided with pads to prevent the loss of lubricant and keep out dust, so that corrosion is prevented at the same time. As a rule the saving in power is over 30%, while the saving in wear and tear of belts and the reduction of repairs are so important that no manager should fail to consider the question of their installation.

Gas pumps in which a liquid plays a part are becoming very popular, and have many practical advantages over fans in some operations, while in addition they provide a simple method of washing the gas. The Nash hydro-turbine pump is a simple pump of this type. The interior of the body of the pump is elliptical in shape, and the only moving part, a wheel or rotor carrying curved teeth or vanes, revolves concentrically in it. Inlet and outlet ports are provided on conjugate diameters of the ellipse so as to communicate with the spaces at the base of the vanes. The liquid, which may be passed through the pump continually if desired, is constrained to follow the elliptical shape of the casing, and in doing so alters the volume of the spaces between the vanes of the rotor. The expanding spaces communicate with the inlet and the contracting spaces with the outlet. The gas, washed as desired, is delivered without pulsation and can be measured in ordinary flow meters. Water, glycerin, sulphuric acid, &c., may be used as the liquid according to the properties of the gas being pumped. Since the pump is self-lubricating, valveless, without gears or reciprocating parts, and has only one single moving part, the rotor, it is very attractive to the chemical engineer.

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[12] U.S. Pat. 1277322; J., 1918, 663A.

A pulsometer pump for corrosive liquids has been patented by A. H. Human and the Kestner Evaporator and Engineering Co., Ltd.[13] It is operated by both compressed air and "vacuum." The chamber, which is alternately filled and emptied, contains a floating ball valve which closes the vessel at the top when full and at the bottom when empty. The opening at the top of this vessel communicates by a pipe with the double valve box connecting to "compression" and "vacuum," and the opening at the bottom connects with a stand-pipe between a suction and a delivery valve. The apparatus appears to be excellent from a practical point of view, and free from the common defects of acid elevators worked by compressed air only.

The drying of air in a simple manner is a very attractive proposition, but the method and apparatus for drying air by compressing it which is patented by F. O. Bynoe [14] would appear to be of limited value and utility. A cylindrical chamber is provided with a loaded "dry" air-escape valve at the top and a long vertical pipe at the bottom with a second loaded valve. The air to be dried is pumped into this chamber, and the separated water accumulates in the long pipe, and its weight finally determines its regular discharge through the bottom loaded valve. The "dry" air escapes through the upper loaded valve. It is obvious that the compressed air must be cooled and that most of the work of compression would be wasted if drying were the only operation to be done.

Considerable attention has been paid to the design of jets for atomising and spraying liquids. An excellent sprayer for scrubbers is that described by I. Hechenbleikner.[15] A central overflow tube closes a large central opening at the end of the sprayer, so that on the spraying holes becoming choked the overflow down this central tube can be observed through a transparent "bell," cover. By removing the cover and lifting the overflow tube the obstructing solids are washed through the central opening at the end of the sprayer.

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[13] Eng. Pat. 115254; *J.*, 1918, 358A.
[14] Eng. Pat. 119590; *J.*, 1918, 723A.
[15] U.S. Pat. 1273856; *J.*, 1918, 643A.

A very simple sprayer, in which slightly compressed air or gas is used, is patented by E. Enke.[16] The gas is fed into the annulus between two tubes, the outer tube projecting beyond the inner tube through which the liquid passes. The pressure disturbance at the end of the jet determines the spraying.

A simple draining device for solids is described by J. M. Whitmer.[17] An endless conveyor belt of filtering material travels on supporting rollers of convex shape. The belt absorbs some of the liquid from the material on it, and deposits it on the rollers as it accumulates near its edges.

The design of scrubbers to wash gases thoroughly without producing serious back-pressure is a problem of continuous interest. Centrifugal spraying washers appear to be as efficient in this respect as any. In a form patented by Kirkham, Hulett & Chandler, Ltd., and S. Hersey,[18] some improvements now appear. Curved scoop-pipes raise the liquid into the rotating perforated trays which produce the spray in each section. A larger annular tray rotates at a lower level and receives the liquid which rebounds from the sides of the scrubber and again sprays it through the gases. In a similar form of apparatus patented by W. B. Davidson and W. C. Holmes & Co., Ltd.,[19] scoop-pipes are also provided to lift the liquid, which is discharged through spraying vanes. Radial ribs on the trays prevent the rotation of the liquid as a whole in each section.

A simple and ingenious plant has been designed by H. Lane[20] for the production of finely divided reduced nickel for catalytic work. A hemispherical pan, heated by means of a gas ring burner, is provided with a vertical central shaft carrying scrapers on arms arranged so as to discharge the material gradually down a central pipe into an oil-bath which also seals the pipe. A continuously sealed hopper, of the rotating plug type, delivers the raw material near the outer edge of the pan. A condenser is connected by pipes to the gas spaces above and below the pan. The reduction is carried out with suitable

[16] Ger. Pat. 304050; *J.*, 1918, 453A.
[17] U.S. Pat. 1279063; *J.*, 1918, 757A.
[18] Eng. Pat. 114370; *J.*, 1918, 291A.
[19] Eng. Pat. 115006; *J.*, 1918, 290A.
[20] Eng. Pat. 115924; *J.*, 1918, 397A.

reducing gas and the progress of the operation is judged by the condensation of water by the condenser.

A retort for the destructive distillation of sawdust has been patented by Blair, Campbell & McLean, Ltd., J. K. Ross, and E. P. Corner,[21] which is of more than common interest. The retort consists of a series of superposed trays with a central vertical rotating shaft carrying arms which move the material round the trays and discharge it through a radial slot in each tray, on to the tray below. The gases given off pass through the space between the shaft and a central hole in each tray. The retort is set in brickwork and heated externally. The design is very simple and is likely to prove successful in good hands.

A few interesting designs in evaporating plant should be noted. In S. Hayek's condenser[22] two concentric cylinders are corrugated circumferentially in such a way as to produce a tubular structure. Gaps are formed in the alternate corrugations, so that a series of tubular rings are formed connecting with each other alternately at the ends of a diameter. The structure is immersed in a casing of ordinary type to hold the condensing water. Such a construction is very ingenious but involves some awkward jointing, and it is certain that a continuous coil of solid-drawn tubing would be more satisfactory for chemical purposes.

An exhaust head for barometric condensers has been patented by J. Tinsley[23] which recommends itself by the injection action induced. The condensing water is discharged through annular jets and through guide cones with serrated edges, so that the streams of water and condensible vapour are intimately mixed.

A simple and rather obvious method of supplying liquid to a still has been patented by J. L. Major.[24] The liquid is discharged on to the surface of that in the still after passing through heating tubes placed in the body of the still. The object is to vaporise the constituents of low boiling-point before mixing takes place with the main body of liquid.

A. L. Webre[25] has given an account of a series of experiments with a simple evaporator of the vertical tube type. He found that the coefficient of heat transmission was a maximum when the static level of the liquid was sufficiently high to keep the heating tubes just wet to the top. In his experimental still with tubes 4 feet high and 2 inches in diameter, this level was from one-fourth to one-third the

[21] Eng. Pat. 118960; *J.*, 1918, 647A.

[22] Ger. Pat. 304602; *J.*, 1918, 613A.

[23] Eng. Pat. 116769; *J.*, 1918, 398A.

[24] Eng. Pat. 114353; *J.*, 1918, 261A.

[25] *J. Ind. Eng. Chem.*, 1918, 10, 191; *J.*, 1918, 254A.

height of the tubes. Under such circumstances no liquid flows down the "down-comers" and no mixing takes place. This would not be satisfactory for some liquids, and it would be necessary to raise the level just sufficiently to provide for adequate mixing. With higher levels the coefficient of heat transmission fell much more than was anticipated. From the diagram given, the fall in the value of the coefficient by making the static level of the liquid at the upper tube plate was over 30%. The author adds a somewhat incomplete but very useful discussion of the design of a quadruple effect evaporator for sugar solutions.

A film evaporator has been patented by T. Blom and A. Gledic[26] in which the liquid to be evaporated is delivered on to a rotating horizontal disc which is heated internally. Warm air is allowed to circulate in the casing which contains the disc, and a scraper removes the dried material at a point just before the fresh liquor is run in.

A heat exchanger designed by A. D. Harrison[27] is used mainly as an oil cooler, but may be used for general cooling or heating purposes. It consists of a series of cast plates arranged as the plates are arranged in a filter press. Each plate is provided with curved partitions on both sides, forming passages through which the liquids pass and having corresponding openings to enable the liquids to circulate from plate to plate. A flat plate is provided between each double-channelled plate. Long bolts hold the structure together, so that it is a simple matter to take the heat exchanger to pieces and examine the plates. As the results of practical tests, it is stated that the cooler for oil has a coefficient of heat transmission of 270 B.Th.U. per sq. foot per hour per 1° F. with a drop of pressure of 15 lb. per sq. inch between the inlet and outlet connections. The heat transmission appears to be proportional to the velocity of the oil, which was nearly proportional to the pressure.

Another heat exchanger of a useful kind with cast elements has been patented by A. H. Bruce and C. Baynes.[28] Each element is an endless circular pipe or ring, with faced inlet and outlet bosses at opposite ends of a diameter. Ring ribs above and below connect the inlet and outlet bosses and semicircular ribs are provided on both sides of the ring ribs, to give a maximum of heating surface. Such elements may be joined together in the same manner as that adopted for the ordinary radiator, or by means of longitudinal bolts.

For cooling corrosive liquids it is becoming a common practice to provide "Field" tubes cast integral with the cover of the vessel containing the liquid. The cooling water is carried to the bottom of the "Field" tubes by the internal tubes, so that any troublesome connections are outside the vessel entirely.

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[26] Eng. Pat. 110753; *J.*, 1918, 755A.

[27] Eng. Pat. 116786; *J.*, 1918, 298A.

[28] Eng. Pat. 118375; *J.*, 1918, 565A.

There are several interesting modifications of filtration plant to notice. Porous unglazed pottery is being more often used. In K. E. Edgeworth's plant for the treatment of peat,[29] filter cones of unglazed pottery are used at a pressure of 600 lb. per sq. inch. In an ingenious continuous filter designed by W. C. Graham,[30] cylinders of porous pottery are mounted on hollow shafts, and revolve at such a distance apart that the deposit which forms on each is rubbed off continually by its neighbour.

A continuous rotary filter deigned by J. A. McCaskell[31] consists of a series of filtering elements carried by a hollow rotating shaft in a closed chamber under pressure. Fixed scrapers remove the solids deposited. In a similar type of leaf filter patented by F. K. and E. P. Atkins[32] the scrapers are mounted on the rotary shaft to remove the solids on the fixed filter plates.

A semi-continuous centrifugal filter has been designed by W. Mauss.[33] The rotating drum which carries the filtering medium consists of two cones which can be separated while the drum revolves. The position of the drum can be altered vertically so that while filtering is taking place the filtrate is discharged into an annular passage in the external casing, but for the discharge of the solids the drum is lowered, the cones separated, and the solids thrown into the bottom of the casing for convenient removal.

A centrifugal separator has been patented by T. H. Parker[34] in which the liquid to be treated is lifted into the separating drum from a tank below. A tube with internal inclined ribs projects concentrically from the base of the separator drum into the tank containing the liquid to be treated. The apparatus ought to be most useful for large-scale work.

A simple siphon which is well adapted for works use has been patented by P. J. Channon.[35] The shorter leg is enclosed in another tube provided with a light foot-valve and a mouth-piece at the top. On dipping it into a tank, the liquid enters through the foot-valve readily. On blowing through the mouth-piece the foot-valve closes and the siphon is primed.

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[29] Eng. Pat. 118903; *J.*, 1918, 645A.

[30] U.S. Pat. 1264635; *J.*, 1918, 400A.

[31] U.S. Pat. 1266133; *J.*, 1918, 454A.

[32] U.S. Pat. 1273127; *J.*, 1918, 566A.

[33] Eng. Pat. 119706; *J.*, 1918, 723A.

[34] U.S. Pat. 1262384; *J.*, 1918, 327A.

[35] Eng. Pat. 112188; *J.*, 1918, 81A.

In a crystallising plant designed by W. G. Adam[36] the hot saturated solution is allowed to fall down a tower provided with glass plates "in staggered form," and up which a current of air is allowed to pass. By the evaporation and cooling of the liquid, crystals are formed during the flow down the tower and are swept by the liquid into a crystallising tank below. Apart from the question of novelty, the plant is ingenious and simple.

A modification of the well-known apparatus and method of comminuting substances which melt easily by feeding them in a continuous film on to a cooled revolving drum from which a scraper detaches the solidified material has been patented by J. W. Leitch.[37] The molten material is fed on to the cooled drum by means of a grooved roller which revolves in it. A screw conveyor is provided for the removal of the solid material detached by the scraper and the whole apparatus is enclosed in a casing which can be evacuated. The use of a feeding roller should be a better method than that usually adopted, viz. to allow the cooled drum just to touch the surface of the molten material and adjust the feed to maintain this condition.

[36] Eng. Pat. 116749; *J.*, 1918, 399A.

[37] Eng. Pat. 117560; *J.*, 1918, 496A.

FUEL.

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Chemistry and Constitution of Coal.

There have not been many new contributions to our knowledge o the nature and constitution of coal published during the year; bu two very important monographs, summarising the present position o the subject, and offering valuable critical comment, have appeared One is Prof. W. A. Bone's book on "Coal and its Scientific Uses"; the other, Dr. Marie Stopes and Dr. R. V. Wheeler's monograph on th "Constitution of Coal,"[2] based on their paper read before the Londo Section of the Society in 1917, and published by the Department o Scientific and Industrial Research. Together, these give a very complete historical account of the chemical work done on this comple subject in three directions: action of solvents, destructive distillation, and action of reagents. The whole review of the action of solvent serves to show that our present knowledge is almost summed up i Wheeler's statement that most coals contain (1) a constituent—probably a degradation product of cellulose—which is insoluble in pyridine and which readily absorbs oxygen; (2) a constituent soluble in pyridine, but insoluble in chloroform, which is probably also "cellulosic' in character; (3) a constituent, soluble both in pyridine and in chloroform, which is probably derived from the resinous portions of th original vegetable matter which produced the coal, and to which i all probability are due the coking properties of coking coals. Thos experimenters[3] who have worked at high temperatures and pressure have usually been able to extract much more considerable quantitie of soluble constituents than those who have worked at more moderat

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[1] *Coal and its Scientific Uses*, W. A. Bone, Longmans, 1918.

[2] *Monograph on the Constitution of Coal*, M. Stopes and R. V. Wheeler, publishe by Department of Scientific and Industrial Research, 1918.

[3] L. Vignon, *Comptes rend.*, 1914, **158**, 1423. F. Fischer and W. Gluud, *Glückau* 1916, **52**, 721. J. Harger, *J.*, 1914, **389**.

temperatures; but an element of doubt exists as to whether the substances extracted at these high temperatures are really constituents of the original coal, or are not rather products of its decomposition by heat. And, again, it is doubtful whether the hydrocarbons which have been extracted by some experimenters, and have been quite definitely recognised and identified,[4] are really constituents of coal in general, or are merely constituents of the particular coal under examination. Indeed, in all work on the constitution of coal, it must not be lost sight of that different coals, even from closely neighbouring sources, have widely differing characters (a conspicuous instance of this is found in the adjacent coalfields of Northumberland and Durham), and that generalisations are premature before work in any given direction shall have been carried out on a great variety of coals.

Further, it is to be noted that all the three " constituents " above referred to appear to contain both nitrogen and sulphur, and that the few analyses which have been made give no certain indication either of the nature of the compounds containing these elements, or of any definite concentration of such compounds either in extracts or in residues. In this connection the statement of Bone,[5] that extraction of a coal by a mixture of pyridine and amyl alcohol has yielded a " resinic " substance free from both nitrogen and sulphur, is of importance, and his more detailed results will be awaited with great interest.

Practically the only new work in this direction published during the year is that of J. I. Graham and J. Hill,[6] who extracted coal (" Barnsley soft seam ") with pyridine in an atmosphere of nitrogen at 40° C. and 60 mm. pressure. They obtained 10–15% of the coal as extract—brown, fusible, about 40% of it soluble in chloroform, and absorbing practically no oxygen at temperatures up to 90° C.; whilst the black, coke-like residue absorbed oxygen as readily as the original coal.

The work on destructive distillation of coal, passed under review in both of these monographs, is vast in extent, and varied in character and in immediate object, and for these reasons no general summary of it is possible. Attention may be drawn, however, to the work of M. J. Burgess and R. V. Wheeler,[7] at home, and of H. C. Porter and F. K. Ovitz,[8] in America, who distilled coals at various temperatures, and found that carbon dioxide and methane, with higher members of the paraffin series, were the chief among the gases first evolved; whilst above 700° or 800° C. the gas consisted chiefly of hydrogen.

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[4] A. Pictet, L. Ramseyer, and O. Kaiser, *Comptes rend.*, 1916, **163**, 358.

[5] *Op. cit.*, p. 93.

[6] *Trans. N. Eng. Inst. Min. Eng.*, 1918, **68**, 37; *J.*, 1918, 262A.

[7] *J. Chem. Soc.*, 1910, **97**, 1917; 1911, **99**, 649.

[8] *U.S. Bur. of Mines, Bull.* 1, 1910.

Whether, as Burgess and Wheeler suppose, this points to the decomposition of two separate constituents of the coal, of differing thermal stability, or whether it simply indicates successive stages of decomposition, with rising temperature, of all the substances present, is not as yet clear; and the work of A. H. Clark and R. V. Wheeler,[9] who carbonised separately the three "constituents" obtained by the action of pyridine and chloroform, whilst it shows that the "cellulosic" portions yield less paraffin and more hydrogen than the "resinic" portion, yet suggests that in all cases there is a yield of paraffins which ceases about 800° C.; whilst, also in all cases, the yield of hydrogen continues to much higher temperatures.

Examination of the results of destructive distillation has thrown little or no light on the nature of the nitrogenous or the sulphur-containing substances in coal.

The action of reagents on coal has so far yielded little intelligible result, though the products of the limited oxidation of coal, whether by nitric acid, by permanganate, or, as in the recent work of Fischer,[10] by ozone, similar as they seem to be to the results of the slow action of atmospheric oxygen, as seen in the "weathering" of coal, are of great interest. A full account of the history of these "Ulmins" is given by Drs. Stopes and Wheeler; and L. C. Maillard's[11] production of "amino-ulmins" by the reaction of amino-acids and sugars, and his production of pyridine bases from them by destructive distillation, together with E. Terres'[12] proof that of all nitrogen compounds only those containing amino-groups will yield ammonia when destructively distilled, form perhaps the beginning of knowledge as to the nature of the nitrogenous constituents of coal.

The history of microscopical examination of coal, and the results achieved by it, given in Drs. Stopes and Wheeler's monograph, will be new to most chemists, and the present writer can do no more than call attention to it; but it is a hopeful sign of future progress in our knowledge of the nature of coal that the chemist and the palæo-botanist should make an allied attack on its problems instead of remaining each in isolation. If it should be possible to separate mechanically. the resinous substances, cuticle, spores and spore-cases, and other elements which microscopic examination reveals, and examine them, or even to ascertain definitely their nature, and subject to separate examination corresponding substances from present-day vegetation, much new light may be thrown on the problem.

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[9] *J. Chem. Soc.*, 1913, **103**, 1704.

[10] *Ber.*, 1906, **49**, 1472; *J.*, 1916, 1001.

[11] *Comptes rend.*, 1913, **157**, 850.

[12] *J. Gasbeleucht.*, 1916, **59**, 519; *J.*, 1917, **586**.

WEATHERING—DETERIORATION—SPONTANEOUS COMBUSTION—STORAGE.

Graham and Hill,[13] in their paper quoted earlier, conclude that the "cellulosic" portion of coal—the residue insoluble in pyridine—is the portion to which is due the deterioration of coal on keeping, and also the heating of stored coal which may lead to spontaneous combustion; whilst the "resinic," or pyridine-soluble portion does not absorb oxygen even at 90° C., and hence "cannot be responsible for the spontaneous combustion" of coal. O. Boudouard[14] and S. W. Parr[15] had long before found that during atmospheric oxidation of coal "humic acids" were formed, presumably from the cellulosic constituents. But as Boudouard found that after this oxidation the coking properties of the coal had disappeared (an observation recently confirmed by G. Charpy and M. Godchot), and as observers practically all ascribe these properties to the "resinic" constituent, it seems probable that this constituent, too, must be affected during atmospheric oxidation.

Some of the workers of the U.S. Bureau of Mines have attacked this problem at different points, and have published some results during the year. S. H. Katz and H. C. Porter[16] passed dried nitrogen over coal at the ordinary temperature, and determined, by absorption and weighing, the water evolved. Incidentally, they found that the loss of weight of the coal was slightly less than the weight of the evolved moisture, as though the coal had absorbed a slight amount of nitrogen. When air was used instead of nitrogen, the coal always gained in weight, showing that it absorbed more oxygen than it lost water; but the alternation of air and nitrogen made no break in the rate of evolution of water. The amount of the evolved water, and also the analysis of the coal after the operation, showed that no water is formed by the oxidation of coal at ordinary temperature, and that the whole of the absorbed oxygen remains in the coal. Later,[17] the same experimenters exposed quantities of 100 grms. of coal in 4½ litres of air at 25° C. for 100 days; whilst the absorption of oxygen amounted to from 279 to 521 c.c., there were formed only from 10 to 43 c.c. of carbon dioxide, and from 4 to 10 c.c. of monoxide. Most of the oxygen remained as such, or in the form of addition-compounds, in the coal. One sample oxidised most in dry, another in moist, air. In regard to the practical question of spontaneous heating, they conclude that natural water in the coal has no effect, and that water actually wetting the coal can act, if at all, only by obstructing the ventilation and thus preventing cooling. It would of course do this most effectually amongst small coal, the segregation of which in storage piles should therefore be avoided.

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[13] See ref. 6.

[14] *Comptes rend.*, 1908, **147**, 986.

[15] *Univ. of Illinois Bull.*, **1908**, No. 17.

[16] *U.S. Bureau of Mines, Tech. Paper* 98; *J.*, **1918**, **199A**.

[17] *U.S. Bureau of Mines, Tech. Paper* 172; *J.*, **1918**, **644A**.

Bone[18] gives a preliminary account of some experiments on the same subject, which usefully supplement Katz and Porter's work. He found that absorption below 80° C. was very slow, but at that temperature increased in rapidity, and at and above 100° C. he found the absorption accompanied by regular evolution of the oxides of carbon and of steam. In about 500 nours, samples of a Durham coking-coal and of Barnsley hard steam-coal, of nearly identical ultimate composition, absorbed, per 100 grms., about 10 litres and 11·7 litres of oxygen respectively. Of this, about 14 % appeared as carbon dioxide, nearly 3 % as carbon monoxide, and about 32 % as steam; so that, roughly, 50 % remained in the coal as "unstable oxygenated bodies primarily formed." Like Boudouard, Bone found that the oxidation had completely destroyed the coking properties of the coal. The inference seems legitimate, from all this work, that the oxidation of coal at low temperatures is not a direct destruction of already existing substances, but a preliminary combination of some of these substances with oxygen, followed by a molecular breakdown in which water and carbon oxides are formed and split off. Bone suggests the possibility of the "activation" of the oxygen by surface-action of some kind as a promoting cause of its absorption.

Some useful technical figures are published by H. C. Porter and F. K. Ovitz,[19] who stored four varieties of sub-bituminous (or lignitic), bituminous, and semi-bituminous coals, in quantities varying from 300 lb. to 120 tons, at several stations in the United States, where the climatic conditions were widely varied, and determined their calorific values, initially and after varying periods of storage. The maximum loss of calorific power of the lignitic coal was 2·3 % of the whole after one year, and 5·5 % after three years; whilst the maximum loss in the case of the other coals was 1·2 % after a year, and 2·6 % after two years. Storage in water, they found, fully protects the coal against loss of calorific power (Zimmer, see below, quotes a coal from Maine, which, after fourteen years' submersion, lost 1·9 % of its calorific value); but in view of the smallness of the figures quoted, they regard it as unnecessary. They think the extent of deterioration during storage has hitherto been overestimated.

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[18] *Op. cit.*, p. 158.

[19] *U.S. Bureau of Mines, Bull.* 136; *J.*, 1918, 615A.

G. F. Zimmer[20] contributes an interesting practical paper to the coal-storage question, though his theoretical basis, derived from Bruigum, hardly commands acceptance. He looks on coal as consisting of: (1) "bitumen," dissolved out by benzene; (2) "humic acid," dissolved out from the residue by caustic soda and precipitated by acids; and (3) "humine," the remainder; and he regards "humic acid" and "humine" as the dangerous portions. He looks on the absorbed oxygen as mechanically held by the coal, and as causing little oxidation unless the temperature rises; but any water present, on evaporation, produces ozone, which causes rapid oxidation—hence warm weather after rain, and sea-air containing ozone, are dangerous. Zimmer suggests screening to separate smalls and dust before storing; and he also recommends storing in pockets or silos with openings at the base. He gives drawings of such bunkers, with a tunnel or gangway at the bottom for the removal of the coal; and a number of diagrams of small-scale experimental apparatus of the same kind showing what happens as the bunker is emptied. If the bunker be properly shaped, and the bottom opening be wide enough, neither small nor large accumulates anywhere, but the average of the content (supposed fairly uniform to start with) runs through. Further, the removal of the coal from the bottom moves the whole pile each time, and favours ventilation.

Several other papers on coal-storage have appeared during the year, but they are chiefly records of particular instances of storage and of the precautions taken to prevent heating or to detect it and counteract it if it should occur, and they present no new feature of interest.

COMBUSTION OF COAL.

The work of H. Kreisinger, C. E. Augustine, and F. K. Ovitz[21] has been continued. Experiments were made with a Murphy stoker, in a furnace with a grate area of 25 sq. feet, and a horizontal tunnel 40 feet long by 3 feet as a combustion chamber. There were 100 experiments, in which three different coals (Pocahontas, Pittsburgh, and Illinois) were burnt at rates of from 20 to 60 lb. per sq. foot of grate area per hour. The volume of combustion space needed depends on the nature of the coal, the rate at which it is burnt, and the volume of the excess air. The gases leaving the fuel-bed contain from 10 to 28 % of combustibles, which represent from 40 to 60 % of the heating power of the coal; and these depend for their complete combustion on a proper supply of secondary air. Completeness of combustion is more nearly reached as the volume of combustion space and the amount of excess air increase, and as the rate of firing lessens. The more volatile matter in the coal, and the higher the proportion of carbon to hydrogen in this volatile matter, the greater the volume of combustion space needed; it seems, indeed, to be proportional to these two factors. Gaseous hydrocarbons, given a sufficiency of air and of combustion space, burn readily: but soot is much more difficult to consume. A source of trouble lies in the tendency for the gases to stratify in travelling along the combustion chamber: the mode of entry of the secondary air should, if possible, be such as to secure mixture, and thus more ready combustion. As the result of their work, the authors consider it possible to design furnaces so that their dimensions shall be the most suitable for given conditions.

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[20] *Engineering*, 1918, **105**, 30 and 57; *J.*, 1918, 81A.

[21] *U.S. Bureau of Mines, Bull.* 135; *J.*, 1918, 328A.

A boiler furnace at a power station is described[22] in which the air, drawn by fans from the neighbourhood of the generators (and thus warm to start with), is passed through a heater, where its temperature is raised to about 110° C. by the spent gases (at a temperature of about 200° C.) on their way to the shaft, and is thence delivered to the furnace; considerable economy is said to be thus effected, and improvement in the combustion of the fuel—especially where this is of low quality.

D. Brownlie[23] contributes a useful statistical paper on coal-saving by scientific control of boiler-plants. The figures given are averages of the actual running of about 250 installations comprising 1000 boilers (935 of which were Lancashire boilers, 36 tubular, and the remainder various). They covered a variety of industries, sizes of plant, pressures (12 to 200 lb. per sq. inch), and descriptions of fuel. The chief figures are: Calorific value of fuel, 11,822 B.Th.U.; ash in fuel, 11·5 %; water evaporated from 212° F., per lb. of fuel, 7·46 lb.; economisers raise feed-water from 116° to 193° F., and cool flue-gases from 598° to 487° F.; saving in fuel by economisers, 7·1 %; carbon dioxide in flue-gases, 7·6 %; steam or power used as auxiliary in producing steam, 2·4 %; thermal efficiency of boilers, 56·71 %; economisers, 4·35 %; superheaters, 0·51 %; and of the whole, deducting auxiliary steam, 60·09 %. The average fuel-consumption was 20·9 lb. per sq. foot of grate area; the author estimates that this might be raised without loss of efficiency to 25–30 lb. (good coal 35, refuse coal 15, coke 22, breeze 15); and that this, assuming a total fuel consumption in the Kingdom in boilers for power purposes of 60 to 70 million tons, and for other purposes of 15 to 30 million tons, would mean a saving of from 45,000 to 60,000 average Lancashire boilers. In only four plants was regular analysis of the fuel carried on; 7 to 10 % might be saved if this were generally adopted, and coal bought on the results of analysis. Of the whole 76 % were hand-fired, with an average efficiency of 57·8 %, and 24% were fired mechanically, with average efficiency of 61·4 %. The superiority of hand or mechanical stoking depends largely on the circumstances of the particular installation, but the author's opinion is that the efficiency in most cases should reach 75–80 %. Only 155 installations were fitted with economisers, and only 80 had any superheating—of these 80 only 25 were fully equipped. The highest figure of saving through economisers was 19 %; but 15 % ought certainly to be reached as an average, whilst the actual figure for the 155 was only 11·4 %. In regard to the carbon dioxide content of the flue-gases, the classification was as follows: Very good (over 12 % of CO_2), 1·6%; good (10–12%), 6·8%; medium (8–10%), 25·6%; poor (5–8%), 57·6 %; very bad (under 5 %), 8·4 %. In only 25 cases was the feed-water regularly measured. The author calculates that with proper reorganisation in the matter of purchase of fuel, measurement of feed-water and check on the working, and more prompt attention to repairs and upkeep, the saving on these 250 plants would amount to 430,000 tons of coal annually; and that if they be taken as typical of average working, the national saving would be 15 to 20 million tons.

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[22] *Engineering*, 1918, **105**, 228.

[23] *Ibid.*, 1918, **106**, 25, and 55.

An interesting feature of the paper is the classification of the various industries concerned, as to the average efficiency of their steam-raising. Paper-mills, explosives factories, and cotton-mills stand at the head of the list, whilst the most wasteful industries are lace-mills, dyeing and bleaching works, and, last of all, collieries. The curious, and not very encouraging, point is also brought out that new installations are by no means always more efficient than old ones.

Firing with coal-dust is being developed, especially in the United States. In an installation for the Missouri, Kansas, and Texas Railway,[24] boilers intended for firing by natural gas and crude oil, were adapted, in consequence of difficulties in the supply of these fuels, to dust-firing. The coal is crushed, passed through a magnetic separator, crushed further, and dried, then ground so that 95% passes a 100-mesh sieve. It is handled by screw-conveyers through dust-proof conduits. If properly dried, the fine stuff moves almost like a liquid, and acts as its own lubricant. The work of crushing, drying, and elevating amounts to 17 h.p. hours per ton. The combustion chamber must be of ample capacity, so that the dust may remain long enough to be completely burnt, and also so that its speed—and hence the cutting-action of the dust itself or of the ash upon the furnace-lining—may be reduced.

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[24] *Engineering*, 1918, 105, 552.

With a properly dimensioned furnace the flame is absolutely smokeless. The best results were obtained with coals containing 40 to 50 % of fixed carbon, 30 to 40 % of volatile matters, and not more than 10 % of ash. But inferior fuel can be efficiently and completely burnt in this way, and perhaps one of the future advantages of dust-burners may be found in their capacity for burning coals containing very high percentages of ash. C. J. Goodwin[25] has suggested the utilisation in this way of the dust from the handling of low-temperature coke; but it may be doubted whether the mechanical properties of this dust will allow it to flow through the conduits and into the burner-nozzles as readily, and with the same freedom from stoppages, as is the case with coal-dust. According to a private communication to the author by Mr. H. Peile, coke-dust could not be burnt in a Bettington boiler unless mixed with about 30 % of coal-dust, and the wear and tear of the boiler was then prohibitively great. Details of burners, and of mixing and combustion chambers, are being worked out by numerous experimenters, and many patents[26] have been taken out for them. The object of all is to secure regularity of delivery and intimate and uniform admixture of coal-dust and air, and control over the proportion between air and dust.

The melting-point of the ash of the fuel is an important factor in boiler-firing, and in all the applications of dust-firing. A. C. Fieldner, with A. E. Hall and A. L. Feild,[27] carried out very careful series of determinations of the melting-points of coals in an electric furnace, in atmospheres of air or steam, of hydrogen, and of mixtures of hydrogen and steam. They found that ashes from fifty different coals varied from 1060° to 1596° C. in softening-point, the average being 1291° C.; and that the average interval between incipient softening and complete liquefaction was 47° C. They further found that whilst the melting-points in air, in steam, or in hydrogen, of any ash differed but little, its melting-point in mixtures of hydrogen and steam (little change occurring with variation of steamcontent from 30 to 70 %) was from 100° to nearly 300° C. lower. They showed this to be due to the iron in the ash, which when oxidised to Fe_2O_3, or completely reduced to metal, exerted but slight fluxing action; but when present as FeO exerted it very strongly. The difference between the melting-points, as ferrous and as ferric or metallic iron, increased with the percentage of iron present; and its average value for fourteen ashes was 202° C. By actual analysis, they found that the iron in ashes melted in steam or air was chiefly ferric; in those melted in hydrogen, chiefly metallic; and in those melted in a mixture of steam and hydrogen, chiefly ferrous In three actual furnace clinkers (the first from a hand-fired furnace, the others from a furnace fitted with a Roney stoker) they found :

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[25] *J.*, 1918, 219T.

[26] H. A. Gill, Eng. Pat. 111412; *J.*, 1918, 3A; J. E. Muhlfeld and V. Z. Caracristi, Eng. Pat. 112115; *J.*, 1918, 83A. G. W. Clendon, U.S. Pat. 1254393; *J.*, 1918, 200A. T. B. Cram, U.S. Pat. 1258654; *J.*, 1918, 292A. A. G. Kinyon and A. I. Jacobs, U.S. Pat. 1258912; *J.*, 1918, 292A. W. D. Wood, U.S. Pat. 1266088; *J.*, 1918, 404A. V. Z. Caracristi and J. E. Muhlfeld, U.S. Pat. 1265172; *J.*, 1918, 404A.

[27] A. C. Fieldner and A. E. Hall, *J. Ind. and Eng. Chem.*, 1915, 7, 399 and 474; *J.*, 1915, 704. A. C. Fieldner and A. L. Feild, *J. Ind. and Eng. Chem.*, 1915, 7, 742 and 829; *J.*, 1915, 1001 and 1079.

Percentage of iron in the clinker.	Percentage of total iron as—		
	Fe.	FeO.	Fe_2O_3.
14·5	12	79	9
12·7	6	75	19
8·9	9	75	16

In this connexion a paper by A. L. Feild,[28] on the melting-points and viscosities of blast-furnace slags, is also interesting reading.

J. T. Dunn [29] determined the melting-points and gave the composition of seventeen different coal-ashes, in an oxidising atmosphere. The results varied from 1020° to 1500° C., a range very similar to that found by Fieldner and Feild. In general, the fusibility showed the same relation to composition as is shown by fireclays, the melting-point being lowered as the percentage of bases—other than alumina—increases.

COKE.

Two communications have appeared from different quarters on the improvement of the coking qualities of coals by judicious admixture. In America, F. K. Ovitz [30] has found that Illinois coal, containing 37 to 46 % of volatile matter, when used in admixture with an Eastern coal of much lower volatile content, in the proportion of 4 parts of the Eastern coal to 1 part of Illinois, produces a much better coke than either separately. Crushing before coking is of great importance with the Illinois coals, as they consist naturally of widely varying qualities in juxtaposition. In France, G. Charpy and M. Godchot,[31] by coking coal, compressed at 5 kilos per sq. cm. into a fireclay tube, in an electric furnace at regulated temperatures, showed that the temperature of coking has an important influence on the mechanical properties of the coke; and that whilst usually the crushing strength increases as the temperature is raised (the figures for 650°, 800°, and 1000° C. being for St. Eloy coal 19·8, 32·9, 38·7, and for Ferrières coal 19·0, 30·5, 45·0 kilos per sq. cm.), this is not always the case (for Noyant coal 100·0, 93·6, 36·3 kilos per sq. cm.), and the proper treatment for each individual coal must be ascertained by experiment. With the Noyant coal, for instance, coking at 650°, followed by gradual rise of temperature to 1000° C., raises the crushing strength of the coke to 130 kilos per sq. cm., whilst the same treatment produces no effect on the St. Eloy coal. Later,[32] these observers have attacked the problem of the mixture of coals. A Brassac coal, containing 11 % of volatile matter, and having no coking properties, was mixed with increasing proportions of a Durham coal containing 24 % volatile, and which made a bulky and spongy coke. Up to 20 % of Durham coal the coke formed had no cohesion. With 25 %, 44 %, 51 %, the crushing strengths were 24, 45, 80 kilos per sq. cm.; but 56 % of Durham coal gave a coke with no strength whatever. The proportions for maximum strength of coke vary, naturally, with the coals used; and they have no direct relation to the percentage of volatile matter in the mixture. Thus the best mixture above contained 19·6 % volatile; but a mixture of Durham and Welsh coals gave the strongest coke (70 kilos per sq. cm.), when the volatile matter was 16 %; and a mixture containing 19 % volatile gave a coke without strength. Charpy and Godchot also found that with a coal like Brassac, admixture of tar or pitch gave it coking properties. When the percentage of tar or pitch was such as to bring the volatile content to 29 or 30 %, a coke standing 130 kilos per sq. cm. was produced. Further, coals high in volatile matter may have their coking qualities improved by heating at a low temperature to the right extent and then coking at a higher temperature; thus a Durham coal yielded the following results on coking at 700° after heating for the number of hours specified at 450° C.:

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[28] *Trans. Faraday Soc.*, 1917–18, 13, 3; *J.*, 1918, 61A.

[29] *J.*, 1918, 15T.

[30] *U.S. Bur. of Mines, Bull.* 138; *J.*, 1918, 568A.

[31] *Comptes rend.*, 1917, 164, 906; *J.*, 1917, 860.

Hours	0	30	60	90	105	120	150	165
Volatile	28·1	23·5	22·2	21·4	20·0	18·1	16·6	14·8
Crushing strength in kilos p. sq. cm.	friable				41	97·6	25·3	pulverulent.

These results, if repetition and extension of the experiments should prove them to be widely valid, may prove of enormous importance to the coking industry, and the work should be closely studied by coke-makers. They are of very considerable theoretical interest too, in view of the question whether or not the "resinic" constituent soluble in pyridine is the source of the coking property, and whether this constituent is the earliest to decompose and give off gaseous paraffins when the coal is destructively distilled.

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[32] *Comptes rend.*, 1918, **167**, 322; *J.*, 1918, 568A.

Two papers on the subject of the mechanical properties of coke, from the point of view of the user, have appeared during the year. G. W. Hewson [33] and G. D. Cochrane [34] have alike emphasised the necessity, for economical working in the blast-furnace, of uniformity, and of a certain minimum hardness in the coke supply. Softness in coke is doubly disadvantageous: it causes the formation of small during the whole handling of the coke before it enters the furnace, as well as during its descent in the furnace itself, choking the draught and slowing, if not stopping, the work of the furnace; and it is more readily, and at a lower temperature, acted on by carbon dioxide with formation of monoxide, and consequent loss of carbon into the waste gases, in which form, even though nowadays it is for the most part utilised, it is still not so valuable as in the form of solid carbon in the furnace. Hewson also points out the desirability of high "available carbon" in the coke, which is equivalent to low ash and sulphur; and the general tendency is noticeable, in coke as in coal-supplies, for the average ash-content slowly to rise as time goes on.

Interesting figures are given by C. J. Ramsberg and F. W. Sperr [35] on the development of by-product coke manufacture in the United States and Canada. The number of by-product ovens at work in 1915 was 6438, and in 1918 was 9900. Though 5000 bee-hive ovens have in the interval been discarded, the amount of coal coked had risen from 24 to 47 million tons, and the yield of coke from 18 to 35 million tons.

The use of coke and coke-breeze in boiler-furnaces is still receiving attention. According to B. Lepsien,[36] either can be burnt in hand-fired furnaces with careful stoking, provided too rapid generation of steam is not required. Chain grates are the most suitable form of mechanically fed furnaces; forced draught is needed with breeze, and even with lump coke, unless the fuel can be pre-heated to near its ignition temperature. Special construction of the arch is necessary so as either to deflect the flame to the front or to increase the radiation upon the front of the fuel-bed, and thus facilitate ignition of the coke. Wirmer [37] has experimented on the addition of coke-breeze to coal on chain-grates. Up to 25 % may be added without making any change in the conditions of firing, but with higher proportions forced draught

[33] *J.*, 1918, 60T.

[34] *J. Iron and Steel Inst.*, 1918, 97, 141; *J.*, 1918, 304A.

[35] Amer. Soc. Mech. Eng.; *Gas J.*, 1918, 141, 440.

[36] *J. Gasbeleucht.*, 1918, 61, 3; *J.*, 1918, 329A

[37] *Z. Ver. deutsch. Ing.*, 1917, 61, 818; *J.*, 1918, 401A.

is necessary. Though breeze alone could be satisfactorily burnt, the best results were obtained with 80 % of breeze and 20 % of nuts. A long and low furnace arch is necessary. Mr. H. Peile tells the writer that he burns coke-oven ballast (which is a poorer fuel even than breeze) quite satisfactorily under a Stirling boiler in a furnace fitted with an appropriate combustion chamber and underfeed stokers. Forced draught under the bars and fan-suction at the base of the chimney are used.

An interesting summary of the work of the Canadian Department of Mines on the utilisation of peat as a fuel is given by B. F. Haanel.[38] The Department carried on for some time the production of peat fuel on a semi-industrial scale. No artificial process of drying was found satisfactory, and the author considers that the manufacture is only possible where natural drying by sun and wind can be carried out. The peat was excavated, pulped in a macerator, spread out to dry, and finally cut into blocks, which contained about 35 % of water. The cost was about 7*s.* per ton with hand-digging, and could have been considerably reduced by using a mechanical excavator. Such low-grade fuel would not bear any considerable transport costs, and would have to be used on the spot, either to manufacture coke and by-products, or to furnish power-gas in a producer, with recovery of ammonia.

LIQUID FUEL.

The importance of liquid fuel for the Navy, and the demand for light spirit for motor and aeroplane work, together with the lessening supply of petroleum in America, have caused a great deal of attention to be given to possible sources, either of natural oil in Britain, or of oils derived from the distillation of coals, cannels, and shales. The increased yield of benzene and toluene from the stripping of town- and coke-oven gas was, during the war, largely devoted to the production of explosives; but probably its value as motor-spirit will result in the continuance of its extraction, and the permanent use (no doubt at a relatively lowered price) of a gas below the present usual statutory limit of calorific value.

A paper by E. H. C. Craig,[39] and a later report of a Committee of the Institution of Petroleum Technologists,[40] review the situation in regard to oil-shales, cannel, torbanite, black-band ironstones, and similar substances. With the necessary labour and means of transport,

[38] *J.*, 1918, 258T.

[39] *J. Inst. Petrol Tech.*, 1918, 4, 110; *J.*, 1918, 175A.

[40] *J.*, 1918, 326R.

about 10,000 tons per day of these substances could be procured, yielding 15 to 80 gallons of crude oil per ton, or, say, 400,000 tons per annum. To work this would only be industrially practicable if residues and by-products could be utilised. Smokeless fuel, either direct or after briquetting, and conversion into power gas, with recovery of ammonia, are suggested as uses for the residues—though the high ash-content of most of these substances would stand greatly in the way of such uses. The Committee rightly urge the need for experiment on a semi-industrial scale to ascertain for each class of substance the best method of treatment and the possibility or otherwise, using such best method, of dealing with the material commercially.

The Petroleum Research Department of the Ministry of Munitions considered this question, and reported on it. A certain mystery enshrouds this report; but from the report of a Committee appointed by the Ministry[41] to consider it, one may gather that the Department recommended the installation of plant on a considerable scale to carbonise these materials, and that one part of this recommendation was the erection of a battery of retorts similar to the small retort at Chiswick, in which their experimental tests of materials had been carried out. The Ministry apparently vetoed the general scheme, and preferred to experiment on the carbonisation of cannel in existing vertical retorts at gas-works; but approved the particular scheme, and are erecting low-temperature retorts at Nottingham, the results from which will be comparable with those yielded by the same material in the vertical retorts at the neighbouring gas-works. These results will be awaited with great interest.

Some results of the treatment of a low-grade cannel (volatile matters 30·35 %, water 2·90 %, ash 9·57 %) in vertical retorts, with admission of steam at the bottom, are given by J. West.[42] The best yields were obtained at a temperature of 1150°–1200° C., lower at the top; 4·78 tons were worked per retort per 24 hours, and gave, per ton, 11,180 c. feet of gas of 541 B.Th.U. calorific value, 20·9 gallons of tar oil, 41 lb. of ammonium sulphate; the crude oil yielded 17 gallons of fuel oil. The corresponding figures for a coal (volatile matters 32·3 %, water 3·3 %, ash 7·6 %) were 3·53 tons carbonised per retort per 24 hours, 14,340 c. feet of gas of 497 B.Th.U., 20·8 gallons of tar oil, yielding 15·1 gallons of fuel oil, and 34·1 lb. of sulphate.

The production of light oils from the heavier fractions of both petroleum and the products of carbonisation continues to be the subject of a great deal of work, and a great many patents have been published during the year on " cracking " processes. But the number of them, and the fact that they nearly all deal with constructional points and exhibit no new principle, make it impracticable, even if it were desirable, to deal with them here ; references will be found in the pages of our Abstracts.

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[41] *J.*, 1918, 325R.

[42] *Gas J.*, 1918, 142, 133; *J.*, 1918, 291A.

The use of tar oil in Diesel engines is treated by H. Moore,[43] who regards practically all tar oils as suitable. The efficiency of tar oils is higher than that of petroleum, and goes some way to compensate for their lower calorific value. Their high ignition point (say, 480° C., against, say, 260° C. for petroleum) causes difficulty, and petroleum or shale oil is often necessary in starting. Heating the cycle air helps combustion, and heating the fuel, as it lowers viscosity and keeps naphthalene in solution, increases the efficiency. Crude tars, or tar oils containing pitch, cause difficulties in working through wear on the exhaust valves, &c. ; these are attributed to the "free carbon" present.

J. H. Willis[44] describes the use of liquid naphthalene in internal-combustion engines. The naphthalene vessel has a jacket through which the exhaust gases pass and keep the naphthalene melted. A proportion of the air is drawn through the naphthalene, and the secondary air comes through an ordinary petrol carburettor, with closed jet. The engine is started on petrol, and when the naphthalene is heated to about 130° C. the petrol is turned off. The temperature of the naphthalene may vary between 130° and 160° C. without any trouble arising with the carburetting.

An important U.S.A. official report, by C. G. Gilbert and J. E. Pogue,[45] of the U.S. National Museum, on the petroleum resources of the States, has been published. Attention is drawn to the rapid diminution in output of the wells and their coming commercial exhaustion, in contrast with the increasing demand for their products. The likelihood of further wells being discovered in quantity sufficient to increase materially the total remaining supply is regarded as very small ; and the steps necessary towards greater economy in usage are discussed and emphasised. Probably one-third of the whole original quantity has been used in less than sixty years, and with the increasing demand a much shorter time will exhaust the remainder. The authors look first to improvements in methods of production and storage, many of which could be effected now if the best-known methods were compulsorily applied everywhere ; then to economies in usage. The

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[43] Diesel Eng. Users' Assoc., May 26, 1918 ; *J.*, 1918, 572A.

[44] *Gas J.*, 1918, **141**, 65 ; *J.*, 1918, 48A.

[45] *Engineering*, 1918, **106**, 633.

"gasolene" and "kerosene" portions are probably already used economically; but the use of the "fuel oil" portion to generate steam is deprecated, and its application in Diesel engines recommended. The production of gasolene by cracking the heavier portions is also desirable. As the supplies of natural oil approach exhaustion, the distillation of shale will become practicable. America possesses enormous supplies of shale, some of it much richer in oil than the Scottish shales, and she will have to look in the future for her supplies of oil to the development of the carbonisation industry.

GASEOUS FUEL.

The importance, in boiler or producer practice, of a knowledge of the amount of total carbon in the fuel used, is insisted on by E. Damour and M. de la Morinière,[46] who point out that it is necessary, and that a knowledge of the fixed carbon and volatile matters only is not sufficient, to enable calculation to be made of the weight or volume of the products of combustion (other than steam), and thus make a balance-sheet of heat-production and consumption. They use a Mahler bomb for the combustion, adapted in the usual way for connection with absorption-tubes.

The reactions of water-gas formation have been studied by Gwosdz,[47] who regards the normal reaction of steam on carbon as $C + H_2O = CO + H_2$. The formation of carbon dioxide is not, he thinks, due to a direct reaction between steam and carbon, but to the reaction between steam and carbon monoxide: $CO + H_2O = CO_2 + H_2$. A water-gas generator of unusual type, utilising these reactions, is described by H. E. Smith and Perry & Co.,[48] the object of it being to vary at will the proportions of carbon monoxide and hydrogen in the water-gas. There are two generators, with a chamber containing limestone between them. In the first stage, air is blown through the generators in parallel; when they are heated, steam is blown in series through the three. It generates water-gas in the first, and the hot gas liberates carbon dioxide from the limestone, which, passing on with the gases into the second generator, reacts on the carbon with production of carbon monoxide. If the proportion of this gas rises higher than is desired, steam can be blown into the second generator, reacting to form carbon dioxide and hydrogen.

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[46] *Rev. Mét.*, 1917, **14**, 789; *J.*, 1918, **143A.**

[47] *Z. angew. Chem.*, 1918, **31**, 137; *J.*, 1918, **539A.**

[48] Eng. Pat. 116582; *J.*, 1918, **456A.**

A report of the Gas Traction Committee of the Petroleum Executive [49] aims at encouraging the substitution of coal-gas for motor spirit. Assuming 250 c. feet of gas to be equivalent to 1 gallon of petrol, then gas at 4*s*. per thousand cubic feet would be equivalent to petrol at 1*s*. per gallon. It recommends that gas undertakings should supply gas for this purpose at their own or at consumers' premises at current prices, and should also allow resale at motor depôts and similar places. Specifications for flexible containers are given, and recommendations are also made for semi-rigid containers of rubber and woven wire for pressures up to about 300 lb. per sq. inch, and for experiment with steel cylinders up to about six times that pressure. No striking new development in these directions has as yet taken place.

A paper by L. C. Harvey,[50] before the Institute of Metals, discusses the relative efficiencies of coke, powdered coal, town gas, producer gas, and oil, in brass-melting furnaces. He puts the efficiency of pit-furnaces at 5 % and of tilting-furnaces at 15 %, the difference being in his view largely due to the higher grade and quicker heating crucibles used in tilting-furnaces. He favours powdered coal, or for large installations producer gas; but his figures for wastage (carried back to the original coal), in the case of coke or of town gas make no allowance for the other products obtained during the carbonisation of the coal required. He draws attention to the need for high-quality refractory materials for the linings of furnaces, and the rapid loss of efficiency when, either through slagging or through abrasion, the lining becomes worn or broken and the contour of the furnace walls is altered. In the interests of economy, the utilisation of the heat of the waste gases from melting-furnaces is an important problem. In the discussion, O. W. Ellis pointed out difficulties in dealing with the ash from powdered coal, and H. Hartley drew attention to the cost of preparing the coal, which made it suitable for large installations only. He drew up balance-sheets for powdered coal, town gas, and producer gas, showing that a ton of the same coal, used in each of the three ways, would, as powdered fuel, melt 15,016 lb. of brass; as town gas, coke, and tar, 13,880 lb., yielding at the same time 35 lb. of ammonium sulphate and 45 lb. of sodium ferrocyanide; and as producer gas, 10,187 lb., with a yield of 85 lb. of ammonium sulphate. Harvey, in reply, objected to this estimate for coal-gas, on the ground that the gas-coke and tar could not be used with the efficiency attributed to them by Hartley, and gave the figure 8214 lb. of brass as more nearly representing what was attainable in practice.

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[49] *J.*, 1918, 186A.

[50] *J. Inst. Met.*, 1917, **18**, 213; *J.*, 1917, 1051.

Further work on the mechanism of gaseous combustion has been published during the year, chiefly by R. V. Wheeler and his colleagues. Wheeler,[51] with W. Mason, has investigated the effect of temperature and pressure on the limits of composition within which mixtures of methane and air will propagate flame. He finds that rise of temperature widens the range, at both upper and lower limit, from 6·0%–13·4% of methane at 20° C., to 3·2%–18·75% at 700° C., the lower limit figures agreeing very well throughout (up to 500° C.) with those of Burrell and Robertson, quoted in last year's report (p. 47). The higher limit figures, at and above 600° C., are probably higher than the truth, for at these temperatures flameless combustion occurs so rapidly as to alter sensibly the composition of the mixture before ignition can be effected. Lowering the pressure at any temperature produces little effect till it is reduced to half an atmosphere; below this the range gradually narrows from both ends, till, at 120 mm. pressure, even the most inflammable mixture will not propagate flame. Raising the pressure from 760 to 4650 mm. gradually widens the range, but by a differential process, the lower limit rising (6·00 to 6·40) as well as the upper (13·00 to 14·05).

In a later paper, W. Payman and R. V. Wheeler[52] find that when methane-air mixtures, contained in tubes open at one end only, are ignited near the open end, the "uniform movement," which is the first phase of propagation of the flame, lessens in speed to a limit of about 35 cm. per second as the tube is narrowed; and with further narrowing the mixture refuses to propagate the flame. The limit of diameter for the most inflammable mixture (9·95 % of methane) is about 4·5 mm., and increases as the mixture deviates from this in either direction. When the tube is long enough for the vibratory period to set in, the vibrations are more violent as the mixture approaches maximum explosiveness; and such a mixture (10% of methane) may be extinguished by its own vibrations where a less explosive mixture, or one of slower speed of propagation (7%), may carry on.

Wheeler[53] also examined the conditions of explosion of mixtures of methane and air, contained in spherical vessels, when ignited at the centre. The maximum pressure obtained was 6·9 atmospheres for a mixture containing 9·8 % of methane, and the pressures dropped symmetrically on either side of this to 2·8 atmospheres for 6 %, and 3·5 atmospheres for 13·9 % of methane. The speeds of propagation of the flame were found to be comparable with those of "uniform movement" in similar mixtures; and indication of rise of pressure at the circumference of the spheres only began after the flame had traversed about one-fifth of the whole volume of the mixture.

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[51] *Chem. Soc. Trans.*, 1918, **113**, 45; *J.*, 1918, 115A.
[52] *Chem. Soc. Trans.*, 1918, **113**, 656; *J.*, 1918, 568A.
[53] *Chem. Soc. Trans.*, 1918, **113**, 240; *J.*, 1919, 3A.

Work on a closely related subject has been done by T. F. E. Rhead,[54] who determined, for various combustible gases, the composition of the "residual atmospheres," *i.e.* the atmosphere in which a flame of the gas in air just burnt itself out, and the "extinctive atmospheres," *i.e.* the atmosphere of air with gradually increased addition of nitrogen which would just extinguish a burning flame of the gas. The residual atmosphere varies slightly in composition with the size of the flame: with methane, for instance, flames of 0·6, 3·0, and 6·0 cm. in height, died out when the percentages of oxygen in the residual atmosphere were 16·8, 15·6, and 14·9 respectively. With different gases, supplied to the jet at equal rates (and under these circumstances giving flames of very varying heights, from 0·6 cm. in the case of hydrogen to 5·0 cm. in the case of butane), the percentages of oxygen in the residual atmospheres were: methane 15·6, propane 15·9, butane 16·0, pentane 16·4, cyanogen 15·3, hydrogen 5·7, carbon monoxide 10·2. The "extinctive atmosphere" depends to some extent upon the rate at which the atmosphere is supplied—increase of this from a rate represented by 684 to one represented by 937, reduced the content of oxygen from 16·6 % to 15·0 %; but for the same speed of gas and the same rate of atmosphere-supply, the first four members of the paraffin series were extinguished by the same atmosphere. With coal-gas, however, the rate of atmosphere-supply has practically no effect on the composition of the "extinctive atmosphere"; whilst the speed of the gas alters it from 13·2 % to 12·3 % of oxygen when the gas speed increases from 514 to 1028 cm. per minute. This appears to be due to the preferential burning of the hydrogen, which with a slow gas-supply is rapidly burnt out and leaves methane, but with a quicker supply is present to maintain the flame even in an atmosphere rather poorer in oxygen.

In connection with the provision of liquid fuel—both motor spirit and fuel oil—as well as of a smokeless solid fuel for domestic purposes, the low-temperature carbonisation of coal attracts much attention, and a useful paper, summarising the history and present position of the subject, was read by E. C. Evans.[55] An essential difference between high-temperature and low-temperature carbonisation of coal arises from the much less steep gradient of temperature between the furnace-gases and the inside of the retort, and the consequent slow transmission of heat through the material to be carbonised. The steps taken to minimise this disadvantage have been in three directions: arrange-

[54] *J.*, 1918, 274T.

[55] *J.*, 1918, 212T.

ment of the retort so that only thin layers of coal are exposed to heat, as in the Tozer retort and the Richards continuous process ; mechanical motion or stirring of the material, as in the Del Monte or " Chiswick " pattern of retort—which is impracticable for use with coking coals ; and internal heating, as in McLaurin's method of heating by hot producer gas. Inasmuch as the yield of gas by any of these methods is very low, and the gas rich in heavy hydrocarbons, and hence not suitable for modern gas-works requirements, the unsuitability of low-temperature carbonisation for gas-works practice is obvious ; and much of the acrimonious controversy which has enveloped the subject and hindered progress by regarding as rivals two processes suited for entirely different ends, has been unnecessary and beside the mark. In most of the experimental plants hitherto erected, the gas has been used to heat the retorts ; but it would probably be remunerative to adopt more severe measures than have yet been adopted for " stripping " it, and adding as much as possible of its content of volatile liquids or soluble hydrocarbons to the light spirit fraction of the liquid products. The yield of these liquid products is considerably greater with low-temperature carbonisation than when higher temperatures are used, and, as is now well known, they contain but small percentages of aromatic hydrocarbons. The light fractions are suitable for motor-spirit, and it has been customary to regard the remainder as fuel oil, though further investigation of the separate constituents may very probably show other, and what may be called " higher-grade " uses for them, especially as they usually contain considerable percentages of phenolic bodies, as well as hydrocarbons. As the solid residue forms usually at least 70 % of the whole, the commercial success of the process largely depends on the value and availability of this. Where the substance carbonised is a coking-coal reasonably low in ash, this residue forms an excellent smokeless fuel for domestic and other purposes, readily ignited, and of high calorific value ; and if the coal be not of a coking character, a similar fuel is obtainable by briquetting the residue. Where the material is a cannel, a shale, or a coal with very high ash, however, the residue will not serve this purpose, and almost the only alternative is to gasify it in a low-temperature producer with ammonia recovery. Were any general system of electric-power distribution established throughout the country, there are many low-grade coals which it would become profitable (or at least economically possible) to work in this way at the collieries, recovering the liquid products and the ammonia, and developing electric power from the producer gas. Small coal, shales, and similar substances, which will not bear the cost of transport, would in many cases become economically workable where they are raised, through the possibility that would then exist of electrically transmitting power; and the high yield of liquid products from low-temperature distillation points to that as probably the most remunerative method of treatment of such substances. The results of the working of the Government plant of "Chiswick" retorts at Nottingham will be awaited with great interest; and the good work that has been done on the small scale by both the Tozer and the Pringle-Richards systems makes it very desirable that opportunity of work on a similar large scale should be afforded to them.

Many variants of the straightforward low-temperature distillation of coal have been suggested, with the object of producing larger amounts of oils—the addition to the coal, for example, of heavy hydrocarbon oils,[56] which become "cracked" during the distillation—or of improving the character of the coke. Most of these last rely upon the application of higher temperature after the products of distillation at a lower temperature have been driven off (*cf.* Charpy and Godchot's investigations on coke, p. 27). Typical of them is "Carbo-coal,"[57] manufactured by distilling coal in a continuous retort, through which it is passed in about an hour, at 480° C. The semi-coked product, after cooling, is pulverised, mixed with pitch, and briquetted, and the briquettes are carbonised at a higher temperature. The coke, containing 4–5 % of volatile matter, ignites readily, and is said to be an efficient fuel in locomotive and marine boilers, whilst the yield of oils and pitch is many times greater than when the same coal is carbonised in a by-product coke-oven.

The report of the Coal Conservation Committee of the Ministry of Reconstruction has been published during the year. The Power Generation Sub-Committee's Report, which was issued in 1917 as an interim report, was noticed in these reports for 1917 (p. 48). The report claims that if the system of national provincial power-stations, which it outlines,[58] were adopted, an annual saving of 55,000,000 tons of coal might be effected. This estimate is based on an average usage throughout the country of 5 lb. of coal per h.p. hour against a usage in the large power stations of the N.E. coast system of 1·5 lb. Points to which attention is drawn are the possibilities of feeding power into the system from local plants utilising surplus gas or waste heat, and of the utilisation at the collieries of inferior fuels which would not bear the cost of carriage. The suggestion of establishing a Board of Electrical Commissioners with power to stop the extension of uneconomical stations for public supply is an interesting parallel to the United States Report's proposal (*ante*, p. 32) to compel economical working of petroleum wells. The reports of the Geological and the Mining Sub-Committees, dealing with the questions of the survey of our national coal-seams, with the establishment of a Ministry of Mines and Minerals, and with the wastage in getting coal, are interesting, but hardly suitable for comment here, save that the remarks on the wasteful consumption of boiler fuel at collieries confirm the statements of Brownlie (*ante*, p. 24). The Carbonisation and Metallurgical Sub-Committee emphasise the need for a complete chemical and physical survey of the British coal seams, and for research on methods of low-temperature carbonisation—both of which they look on as the work of the Fuel Research Board; and they suggest that progress will be best effected by examining the application, first of the best known methods, and then of new methods, to the present output of marketable coals, and then applying these methods to "possible products of the coal-mine, which at present are either neglected or wasted." They do not discuss at any length the gas industry, in view of the facts that it is at present in an abnormal condition owing to the conditions imposed upon it by the War, and that the Fuel Research Board, at the request of the Board of Trade, are already pursuing inquiry and research in regard to it. Their remarks on the coke industry, and its relation to fuel economy in iron and steel manufacture, are chiefly based on two reports, by Prof. W. A. Bone and Mr. B. Talbot respectively, given in full as appendices. The prejudices against by-product coke are said to be now rapidly dying out, and the figures quoted in the report seem to bear this out; for, in 1916, out of 20,000,000 tons of coal used to make coke, nearly 15,000,000 was carbonised in by-product ovens, or three-fourths of the whole. The yields calculated from these figures are rather striking: 20·1 of total coal yielding 13·4 of total coke, or 66·7 %; whilst 14·6 of coal in by-product ovens yielded 10·6 of coke, or 72·6 %, and hence by difference 5·5 of coal in non-recovery ovens yielded 2·8 of coke, or 51%. The number of recovery ovens in Britain, working or ready for work, in November 1917, is given as 8700, with an estimated output of 12,250,000 tons of coke from 17,500,000 tons of coal. A similar estimate for the United States gives 25,000,000 tons of coke: a figure which may be compared usefully with those given by Ramsberg and Sperr (*ante*, p. 29) for the United States and Canada. For the economical working of the iron and steel industry the establishment of large self-contained units, capable of turning out annually 300,000 to 500,000 tons of steel, is advocated; the coal needed is to be coked at the works and not at the colliery, so that the blast-furnace gases may be utilised to heat the ovens, and allow the use of the rich coke-oven gas of high calorific value for the steel-furnaces. It is claimed that with proper arrangements no coal need be used beyond that which is coked for the blast-furnaces, and full details in support of this claim are given in Mr. Talbot's report. Economies beyond those which have already been achieved are suggested in the utilisation of the heat of the coke as it leaves the ovens, and that of the slag from the blast-furnaces. Two questions for consideration are mentioned in the report: one is the desirability or otherwise of stopping the export of coking-coal, in view of the limitations of the supply, and especially in view of the fact that much is exported for bunkers and similar purposes for which non-coking-coal would be equally suitable. This point is, of course, connected with research on the nature and cause of the coking property, already frequently mentioned in these pages (*ante*, p. 27). The other is the desirability or otherwise of coking all the coal (whether by high or low temperature carbonisation) used for power-production in the kingdom, and of firing boilers with, or using in gas-engines, the gas produced by the carbonisation, and that yielded by the gasification, in producers, of the coke. It is generally admitted that this is a moot point, and exhaustive research on the subject should have the early attention of the Fuel Research Board. Meanwhile the Power Generation Sub-Committee in their recommendations urge that the sites of stations should be so chosen that land would be available for the erection, if found advisable, of by-product carbonisation plant as well as of the power plant. Interesting diagrammatic illustrations of possibilities in this direction will be found in some of the patents [59] already taken out with this object.

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[56] G. E. Heyl, Eng. Pat. 113012; *J.*, 1918, 177A. F. C. Blythe, Eng. Pat. 113079; *J.*, 1918, 177A. F. M. Perkin and J. West, Eng. Pat. 114937; *J.*, 1918, 295A.

[57] W. Savage, *Chem. and Met. Eng.*, 1918, **19**, 579; *J.*, 1918, 679A.

[58] *Ann. Rep.*, 1917, **2**, 48.

A final recommendation of the Carbonisation Sub-Committee, and perhaps one of the most important from the fuel economy point of view, is the provision, not only in coke works and steel works, but in all industrial concerns using fuel on any scale, of a staff of trained fuel experts to control the fuel consumption. This has from time to time been insisted on by those whose work it has been to survey installations of any magnitude using fuel (see, for example, Brownlie, *ante*, p. 24); perhaps the repetition of the utterance by a body so disinterested and of such importance as the Coal Conservation Committee may lead to its consideration by fuel-users in some number. Those who adopt the recommendation will never be likely to revert to the ***status quo ante—expertum.***

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[59] Merz and McLellan and others, Eng. Pats. 117290 and 118777: *J.*, 1918, 499A and 646A.

GAS—DESTRUCTIVE DISTILLATION—TAR PRODUCTS.

By Alwyne Meade, Assoc.M.Inst.C.E.,
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The Components of Town's Gas.

So far as the year 1918 was concerned, it is pleasing to be able to record that the gas industry, though handicapped by unmerited hardships and commercial disappointments, continued to make progress in its appreciation of that valuable relation which exists between scientific principles and the economic prosecution of industry. There is evidence on every hand that the members of the carbonisation industries are learning to recognise more and more that the rule-of-thumb methods of the past century were not worthy of a process which contains such unlimited possibilities, the result being that scientific and practical co-ordination has come to be regarded as a *sine quâ non* in the present quest for the ideal. Discussion, in the main, has ranged round two outstanding problems—namely, the most effective method of dealing with raw coal in order that its potentialities shall be utilized to the utmost, and the definition of those physical properties of coal-gas which are of essential service to the consumer; consequently, the specification of a standard quality of gas which will best fulfil this purpose. As must be expected, these problems are such as to demand the most careful scrutinisation from all points of view, as has been shown by the guarded report, issued in August 1918, of the Coal Conservation Committee[1] and the sub-committees which were appointed by it. Developments in the gas industry are conditioned to a great extent by the fact that the right to distribute "town's gas" is a monopoly secured by Acts of Parliament and hedged round by the imposition of certain fixed standards of quality and price. Any proposed improvement in the processes or apparatus employed in its manufacture has, therefore, to be considered very closely from the point of view of the Acts of Parliament and the standards and responsibilities involved in the supply of this particular product. Meanwhile, the Fuel Research Board has continued to progress with the erection of its central research station at East Greenwich, the director—Sir George Beilby—being responsible for the lay-out and equipment of plant,[2] the first portion of which is to cost about £120,000. The scheme of research which it is proposed to carry out at this station is expected to have an important bearing upon future developments, and from the results obtained it is hoped that the way may be prepared for the consideration of post-war reconstruction.

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[1] *Coal Conservation Committee's Report*, Cd. 9084, Aug. 1918.

The whole aspect of gas constituency has been modified by exigencies imposed by the war, with the result that the archaic beliefs associated with intrinsic luminosity have universally come to be regarded as *in articulo mortis*. With the passing of the old standard, calorific power has for the time being taken its place as the standard of judgment, but the original figure of 500 B.Th.U. has undergone reduction until now 450 B.Th.U. has been prescribed as the minimum.[3] The opinion has been growing, however, that calorific power *per se* is by no means the only factor which must be taken into account when standards of quality come to be prescribed, for where gas employed for industrial purposes is concerned, there are other properties which have, possibly, very much greater significance. Bone[4] has stated, for example, that important functions, which depend in high degree upon chemical composition, are (*a*) density, (*b*) the range of explosibility, and the ratio of back-firing of mixtures of a given gas and air, (*c*) flame temperature and combustion intensity, and (*d*) the radiative power of the flame produced. There is manifest an increasing tendency to give flame temperature a priority of calorific value, and the fact that a high value of the latter property is not followed by improved results in the way of calorific intensity has been instrumental in advancing the case for the admixture of straight water-gas with coal-gas, the water-gas being produced either from separate units or by the steaming of the coal-charge. Indeed, the value of water-gas as an auxiliary has been shown by the following experimental figures:[5]

	Calorific power per cub. ft. at 0° C. and 760 mm.		Observed max. flame temp. in air °C.
	Gross.	Net.	
Hydrogen . .	343·3	287·2	1900
Coal-gas . .	560	500	1871

According to Bone, the calculated mean flame temperature of hydrogen is 1918° C.; carbon monoxide, 1700° C; methane, 1670° C. ethylene, 1900° C; acetylene, 2322° C.

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[2] *Report Com. Scientific and Ind. Research*, 1918.

[3] *Def. of Realm Regs.*, *Reg. 8g*, June 28, 1918.

[4] "*Coal and its Scientific Uses*," 253.

[5] *Ibid.*, 264, 266.

The first report[a] of the Gas Investigation Committee of the Institution of Gas Engineers has indicated that the research remaining to be carried out before any definite line of policy can be laid down is considerable. In order, in their preliminary work, to obtain useful information in a limited time, the committee has made a rapid survey of three important domestic applications of gas—that is, through the ring-burner, the incandescent mantle, and the gas-fire.

Comparative boiling tests relative to efficiency have been carried out by employing a number of gases of variable composition, by modifying the distance between the heated vessel and the burner, and by consuming the gas at different rates. The conclusions to be drawn from the tests may be summarised as follows:

(1) Within the limits examined, the efficiency does not depend upon the time taken to raise the temperature.

(2) Unless interfered with by poor aeration or by too close proximity to the containing vessel, the efficiency is almost independent of the rate at which the gas is burned between the limits 10 to 25 cubic feet for this burner.

(3) Flame contact is essential for high efficiency, and should be as complete as possible, consistent with proper aeration and ventilation of the burner.

(4) The distance of the base of the vessel from the burner requires careful consideration, if the maximum efficiency is to be secured.

(5) Any factor (such as modification of the composition or calorific power of the gas, degree of aeration, or rate of consumption) which alters the size and shape of the flame, is equivalent in effect to altering the distance between the bottom of the vessel and the burner.

(6) Poor aeration is not always a disadvantage from the thermal standpoint, but there is always the risk of objection upon hygienic grounds.

So far as the determination of the composition of a gas most suitable for the purpose is concerned, the preliminary conclusions of the Committee have shown that, as regards that common appliance, the ring-burner, it is possible to utilize different grades of gas embracing a wide variation in the way of constituents without impairing efficiency. This conclusion, if it is corroborated by future work, is important in that it denotes that, as this appliance gives practically equivalent results with all practicable gases, it may be left out of the reckoning when a model gas for the many other appliances comes to be considered. In view of the importance which is to-day attached to flame temperature, it is interesting to note that, so far as the process of heating water over the ring-burner is concerned, the effect of flame temperature, when it varies within practicable limits, is negligible. This has been ascribed to the fact that the difference between the temperature of the water in the vessel and that of the flame of any gas mixture which has been experimented with is so great that the normal variation in flame temperature does not make itself felt.

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[a] See *J.*, 1918, 68 A.

In 1917, G. Helps[7] introduced the idea of admixing with the coal-gas at the works a sufficient quantity of air, so that calorific power is reduced to as low as 350 B.Th.U. net. Dealing with suggestions of the kind, the Gas Investigation Committee[8] reported that the addition of air to gas at the holder does not, so far as the ring-burner is concerned, give better results than those obtained with a properly adjusted burner working in the ordinary way, whilst pressure required to deliver the same number of heat units and to do the same heating is increased.

The Committee has also drawn up preliminary conclusions with regard to the most suitable mixture for employment in upright incandescent burners and in gas-fires. Their conclusions are too diffuse to receive detailed mention in this report, but it may be pointed out that, briefly, with the incandescent burner the following points are of chief concern :

(*a*) The zone of active combustion must be made to fit the mantle, and so long as this requirement is fulfilled the question of flame temperature becomes relatively unimportant.

(*b*) A gas of from 500 to 550 B.Th.U. gross gives the best performance. Gases of 600 B.Th.U. give inferior results owing to defective aeration, while those below 450 B.Th.U. are unsatisfactory owing to difficulty of control.

Again, with regard to the work carried out with gas-fires, the following considerations are worthy of notice :

(*a*) If a fire is turned down so that less than half the radiants are heated, efficiency suffers severely.

(*b*) Evidence so far obtained points to the conclusion that no very considerable difference in radiant efficiency occurs when different grades of gas are used so long as the construction of the fire permits of the requisite quantity of heat units per hour being supplied to the radiants. At the same time it is to be noted that existing gas-fires vary very considerably in their ability to adapt themselves to different grades of gas.

[7] *Annual Report*, 1917, p. 55.

[8] *Gas World*, 1918, 69, 223.

Inert Constituents.

Any depreciation in the quality of coal-gas which may have been noticeable for the past year or so must not be entirely attributed to war's demands but to war's contingencies, for the majority of gasworks have been carrying on under difficulties in regard to the supply of raw materials and labour, which have probably been more pronounced than in any other industry. There can be no doubt that the real cause of any deterioration has been the necessity for extracting every ounce of gas from each ton of coal, and as carbonising plant has had to forgo the usual repairs, there has followed an increase in the incombustible constituents which have in certain cases[9] attained twice the pre-war proportions. That even inert constituents have their uses, however, is shown by a statement made by Sir Dugald Clerk, who, in speaking of the desire of some gas-engine builders to obtain a higher cylinder compression, stated that the pre-war variety of gas was of too rich a nature in that high compression was inevitably followed by spontaneous pre-ignition. Thus, when it came to building engines of 3000 h.p. and upwards, it was necessary to lead back a portion of the waste gases to the cylinder; in other words, to add inerts by artificial means. This, in effect, is the application to the gas-engine of the 'poisoning' effect which carbon dioxide has upon pre-ignition. Sir Dugald Clerk,[10] however, was essentially speaking from the point of view of power users, who represent a consumption of only 10% of the total gas manufactured in the country.

Gas as a Furnace Fuel.

Hartley[11] has stated that, if in the ordinary metal-melting furnace the hot gases could be made to impinge upon the metal itself, a more rapid and efficient heating-up would be obtained, and although there appears to be a limit to this procedure, advantage has been taken of it in the pre-heating of the metal in the most efficient types of furnace made at present. Commercially, it has been found practicable to save 30% of the fuel bill by proper attention to pre-heating.

R. A. Hadfield[12] has alluded to the fact that at the works of his company in Sheffield, 360 million cubic feet of coal-gas and 3,780 million cubic feet of producer-gas were consumed in 1917. He has given the following practical figures of fuel consumption, which have been obtained in actual work:

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[9] *Engineer*, October 26, 1918, p. 354.

[10] *Gas World*, 1918, 69, 227.

[11] *J.*, 1918, 65R.

[12] *J.*, 1918, 241R.

To heat 1 ton of steel to 900° C.

	Fuel or energy consumed.	Heat efficiency.	Equivalent tons of coal.
Coal . . .	0·08 ton.	23%	0·08
Gas . . .	2750 c. ft.	32%	0·23
Electricity . .	300 units.	54%	0·38

In view of the growing tendency to admix blue water-gas with coal-gas, and the consequent increase in carbon monoxide content which occurs in the product as distributed, it is interesting to refer to the remarks of Bone,[13] who, in dealing with the use of gaseous-fired furnaces, points to the increased value of carbon monoxide as compared with hydrogen, owing to the fact that the flame of the former gas has a radiative power equivalent to 2·6 times the radiative capacity of the hydrogen flame. To this reason may be assigned the fact that those accustomed to work with open-hearth steel furnaces invariably prefer a producer-gas rich in carbon monoxide and with a low hydrogen content. C. Johns[14] has pointed out that not only is carbon monoxide to be preferred for this reason, but it has a less detrimental effect than has hydrogen on the walls of the furnace.

Decomposition of Hydrocarbons.

J. W. Cobb has continued the valuable work which he has been carrying out at Leeds University in connection with the thermal degradation of the hydrocarbons evolved from coal in the retort. In his most recent work he has studied the mode of decomposition of single constituents, chief attention having been given to benzene and toluene. In his earlier work Cobb studied the behaviour of benzene when admixed with hydrogen and methane—that is to say, when subjected to an atmosphere closely approaching that of the retort. These experiments indicated the stable nature of benzene at low and moderate temperatures and its complete instability at higher temperatures. At 800° decomposition was negligible, but at 1100° the gas, which had originally contained 5% of benzene, 47·8% of methane, and 47·2% of hydrogen, was found to contain no benzene, 11·1% of methane and 88·4% of hydrogen, with a trace of acetylene.

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[13] *"Coal and its Scientific Uses,"* 262.
[14] *Proc. Iron and Steel Inst.*, Sept. 1918.

An endeavour has now been made to develop a process for the production of toluene from coal, an essential preliminary being the solution of the problem of how benzene and its homologues decompose under the action of heat, due attention being given to the special conditions attaching to the carbonization process. In the first instance it was found[15] that, in a stream of nitrogen rich in benzene, decomposition just started at a temperature of 550°, and at this stage a solid resembling naphthalene was deposited. This was identified as diphenyl and was produced in increasing quantities, together with hydrogen, as the temperature was carried higher. At still higher temperatures, however, decomposition went a stage further, diphenylbenzene being found. These results are a little perplexing in that, although benzene is found in some quantity in coal-gas and tar, diphenyl is present in quantities scarcely sufficient to be separated. Here is an instance of the so-called differences between theory and practice, or, between laboratory and large-scale results, indicating that some important factors had not been taken into account. The discrepancy was, however, ascribed to the prevailing atmosphere, or the state of dilution of the benzene by other gases, notably hydrogen and methane. When experiments were repeated, in which the benzene was highly diluted with nitrogen, decomposition was lessened, and the yield of solid condensates, such as diphenyl, decreased. Hydrogen was then employed in lieu of nitrogen as a diluent. By gradually diluting further and further with hydrogen, the quantity of molecular condensates gradually diminished until, when the benzene was reduced to a proportion of about 8% by volume of the mixture, only traces of diphenyl were produced, the benzene being practically undecomposed by the treatment. A reason was, therefore, clearly established for the stability of benzene during carbonization at such temperatures as 800° C. At higher temperatures (900°) benzene was found to be readily decomposed, even when highly diluted with hydrogen, and deposition of the characteristic grey methane carbon was noticed. When the temperature was raised to 1100° C. with an atmosphere imitative of carbonising conditions, benzene disappeared entirely, as was found in the earlier research.

Further experiments were made with toluene. In this case, when decomposition occurred at 600° C., the solid condensate produced was found to be stilbene. At the same time an oily substance was formed. At higher temperatures increasing decomposition was noted, and at 750° C. it was quite extensive. The most noteworthy distinction from the behaviour of benzene, however, occurred when a hydrogen atmosphere was employed, for it was found that the decomposition of the toluene was very much accelerated, with the production of large quantities of benzene, and smaller amounts of solid condensates. What happens, then, is that the hydrogen atmosphere can act directly on the toluene producing benzene and methane.

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[15] *The Times, Eng. Supplement,* Oct. 1918, 205.

The decomposition of the xylenes was found to be very similar to that of toluene, yielding, in an atmosphere of hydrogen at 750° C., toluene and benzene by reduction, and a limited quantity of solid condensates. Cresol is also reduced extensively (at 750° C. in hydrogen) to toluene and, necessarily, to benzene also.

The conclusions set out above clearly indicate that there is a tendency for hydrogen, which is the predominant product of carbonisation, to reduce the single-ring benzene compounds to benzene, but at the same time to preserve the benzene nuclei intact. A similar action of hydrogen on the attached groups of more complicated ring compounds most probably accounts for the production of naphthalene and anthracene. Hence the formation during high temperature conditions of the horizontal retort of a considerable quantity of the aromatic hydrocarbons and naphthalene, with a corresponding decrease in the yield of paraffins and phenols.

W. R. Hodgkinson[16] has studied the reactions and decomposition of acetylene, and summarises the behaviour of this hydrocarbon when in contact with various metals. He states that acetylene may be passed at a moderate speed through a glass or silica tube heated to 600°–800° C., either alone or diluted with nitrogen, hydrogen chloride, or with coal-gas, for from 20 to 60 minutes before any serious decomposition occurs. The nature of the glass has a decided influence on the rate of decomposition. Silica has less effect than has soda-glass.

Recovery of Original Calorific Power of Coal.

Bedson[17] has given figures representative of the heat distribution in the products of distillation in ordinary gas retorts. The heat in 100 lb. of dry coal was distributed thus: In saleable coke, 47·8%; in coke used for heating retorts, 11·4%; in tar, 6·1%; in saleable gas, 21·3%; in liquor, sulphur, and loss, 13·4%.

As an instance of the manner in which the original calorific power of coal is distributed after carbonisation, the following table,[18] which relates to statistics obtained from 8,500,000 (metric) tons of coal distilled in Germany, is instructive in that it relates to results on a large scale :

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[16] *J.*, 1918, 86T.

[17] *Gas World, Coking Supplement*, Feb. 2, 1917, 16.

[18] "*Die Wirtschaft der Deutschen Gaswerke*," 1914, 14.

	Percentage by weight of coal carbonised.	Percentage of heat units recovered from original coal.
Gas (made) . .	17·5	24·0
„ (sold) . .	(16·6)	(22·8)
Coke (sold) . .	56·0	67·0
Tar . . .	5·0	6·0
Ammonia . . .	12·42	—
Cyanogen . . .	0·02	—
Retort carbon . .	0·06	—

Atmosphere in Vertical Retorts.

The modern vertical retort lends itself admirably to an adjustment of "atmosphere." This fact has led to important attempts to modify both liquid and gaseous products by adjusting the conditions of atmosphere in accordance with the results desired. Hydrogen may be readily brought into the retort, either in the form of de-benzolised coal-gas, as blue water-gas, or by the generation of water-gas *in situ* by the injection of steam. J. W. Cobb[19] has said that the action of a scouring gas in the retort may be regarded in two ways. Even an inert gas, such as nitrogen, would not be without effect, because it would wash the volatile products out of the pores of the coke, assist their volatilisation by lowering their concentration in the vapour phase, and hurry them away from the region of decomposition. So light a gas as hydrogen has a great power of diffusion, and it is, therefore, even better able to penetrate the pores and perform these duties. The general effect of the ascending stream of gas to be anticipated is that of increasing the yield of gas and of the lighter constituents in the tar. In so far, however, as the secondary products of carbonisation are concerned (in which are included benzene, toluene, and other valuable products for the manufacture of dyes and drugs), the plant which excels in the rapid removal of products without any considerable decomposition may have its disadvantages. The suggestion is made, therefore, that carbonising plant might be so modified that, whereas conditions would prevail which would ensure a high yield of gas and paraffinoid condensed products, the gas should be accorded secondary heating, which would ensure the volatile hydrocarbons being obtained in the benzenoid form.

The tendency for paraffins to predominate when ordinary grades of gas-coal are employed in continuously operated vertical retorts, has prompted Perkin and West[20] to develop a system by means of which the hydrocarbons, particularly those remaining in the tar, may, if desired, be transformed largely into the benzenoid variety. The method, it is claimed, provides a means whereby a higher yield of coal-tar and of low-boiling aromatic hydrocarbons may be obtained under high temperature conditions, with a corresponding diminution of hydrocarbons of the aliphatic series, the presence of the latter in the lower fractions of the tar adding to the difficulty of purifying the benzol and toluol. Perkin and West state that if a gas of moderately low quality—such as "stripped" coal-gas—be passed into the lower end of the retort at such a rate that it is able, after traversing the incandescent coke zone, to carry the volatile matter from the partially carbonised coal through the relatively cool coal (which is just entering the hot zone of the retort) without the volatile matter becoming condensed in the cool coal in any degree, then, not only is the amount of tar distilled increased in volume, but its specific gravity is decidedly lower. In this process the stream of low-quality gas is admitted beneath the coke-extractor worm, and as the rate of supply of the subsidiary gas is of importance, it is regulated by increasing the vacuum exerted by the exhausters on the main gas-outlet, or by admitting gas under pressure. The tar is found to contain an additional proportion of benzene, toluene, xylene, and phenols, with a corresponding diminution in the yield of paraffins.

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[19] Wm. Young Memorial Lecture, Sept. 1918.

Steaming the Coal-Charge.

The success which has attended the process of steaming the charge in vertical retorts has led to many attempts to apply the same system to horizontal retorts. A certain amount of success has been obtained in the latter direction, but, on the whole, it may be said that, unless highly superheated steam is employed, derangements, such as the reduction of working heats or the excessive deposition of water, are likely to follow. The most favourable results have been obtained by working the horizontal retort on semi-continuous lines. That is to say, one ascension pipe is stopped and steam is admitted from that end of the retort. Instead, as is customary, of discharging the whole of the coke at one operation, only half of it is pushed out at a time, (the remaining half filling that portion of the retort which is adjacent to the steam supply), while the cleared half is re-charged with coal. After the usual period of distillation the charge (now reduced to coke)

[20] *The Times, Eng. Supplement*, June 1918.

is similarly pushed forward, and its place is taken by a further supply of coal.

The procedure of steaming the charge in continuous vertical retorts has been generally adopted, and has had an important effect in conserving supplies of coal at so difficult a time. J. West,[21] experimenting with Orrel nuts and steam supplied at 40 lb. per square inch pressure through a ⅛-in. nozzle, has given the following figures: Make of gas per ton of coal (corrected to N.T.P.), 16,607 cubic feet; illuminating power (No 2 Met. burner), 8·34 candles; calorific power, gross, 505 B.Th.U.; calorific power, net, 459 B.Th.U.; coke yield per ton of coal, 13 cwt.; tar yield (dehydrated) per ton of coal, 20·0 gallons; ammoniacal liquor (10 oz. strength), 43·9 gallons. The remarkable effect of steaming upon tar and liquor yields will be appreciated when it is mentioned that with the ordinary methods of horizontal retort carbonisation, the normal yield of tar is 11 gallons, and that of liquor 30 gallons.

Hislop[22] considers that the greatest difficulty met with in steaming is that of curtailing the carbon dioxide content of the gas so as to bring it within reasonable limits. He has succeeded, however, in increasing the temperature of the lower sections of the retorts sufficiently to give a yield of nearly 18,000 cubic feet of gas per ton, the gas containing under 4% of CO_2. It is instructive to note that, although he has obtained over 2 gallons of benzol per ton of coal carbonised, this product contained a large proportion of paraffins. West is inclined to think that for steaming purposes a ⅛-in. nozzle and a steam pressure of 40 lb. should be used in general, although it is necessary to be guided by experiments with the various kinds of coal carbonised.

An idea of the increased volume of gas which may be obtained per ton of coal by the employment of steam is given by the following table, which has been compiled from results obtained by J. West[23] with Orrel nuts:

	Without steam.	With steam at 25 lb.	With steam at 40 lb.
Gas, per ton of coal (cub. ft.) .	14,989	17,759	21,684
Calorific power (gross B.Th.U.) .	503	460	442
Tar, per ton (dehydrated), galls.	17·4	18·2	18·6
Liquor (10 oz.), per ton, galls. .	39·7	42·4	40·3
B.Th.U. (gross), per ton of coal .	7,538,461	8,169,140	9,584,328

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[21] *Proc. Southern Association Gas Eng.*, Nov. 1917.

[22] *Ibid.* (J. West's paper), 15.

[23] *Gas J.*, 1917, 140, 563; *J.*, 1918, 26A.

Benzene and Toluene.

An order[24] was issued by the Minister of Munitions, in June 1918 to the effect that all gasworks which have facilities for scrubbing the coal-gas must treat the gas produced to the fullest possible extent for the extraction of ammonia, benzene, and toluene. In some cases not only is the coal-gas subjected to the process of washing with green oil when in its purified state, but after passing the ammonia scrubbers it is also treated with tar. Thus the "C" process and the normal oil-stripping processes are applied to the same gas.

As a comparison between pre-war practice, the "C" tar-washing process, and the oil-washing methods now employed, the following figures[25] are of interest:

	Pounds per ton of coal carbonised.	
	Benzene.	Toluene.
Originally recovered from tar . .	0·4	0·130
Recovered by tar-washing process. .	1·5	0·75
,, ,, oil-washing process . .	10·0	3·50

J. West[26] states that, taking a number of tests which have been made on vertical retort tar, it is found that, by average, the tar contains 0·7% of benzene, 0·3% of toluene, and 0·3% of paraffins. On the other hand, with horizontal retort tar an average result is, approximately, 1·4% of benzene, 0·5% of toluene, and a slight trace of paraffins. West also gives the approximate quantity of benzol and toluol (crude spirit) obtained per 12,000 cubic feet of gas as follows: In vertical retorts—benzol 4·5 lb., toluol, 1·6 lb.; in horizontal retorts—benzol, 9·0 lb., toluol, 4·0 lb.

Although vertical retorts give less hydrocarbons of the benzene series and more paraffins than do "horizontals," it has to be remembered that a larger quantity of fuel oil is obtained from the former. The figures for fuel oil for the two systems have been given by Colman as 7¾ gallons and 3 gallons respectively.

With regard to the effect of extraction on the quality of coal-gas, it has been stated[27] that the loss in calorific power approximates to 4·5% when 2·1 gallons of crude spirit is extracted per ton of coal, 7·0% when 2·5 gallons is extracted, and 8·0% when 3·0 gallons is extracted.

L. J. Willian[28] states that in America the average yield of light oils is about 3 gallons per ton of coal carbonised, but this undoubtedly refers

[24] *London Gazette*, June 28, 1918.

[25] *Proc. Inst. Civil Eng.*, March 1918.

[26] *Gas J.*, 1917, 377.

[27] *Proc Inst. Civil Eng.*, March 1918.

[28] *American Gas Inst. News*, Dec. 1917; *J.*, 1918, 199A.

to the gas produced from coke-ovens. He states that the light oils recovered have approximately the following composition: Benzol 50–60%, toluol 12–13%, solvent naphtha 10–12%, heavy naphtha and wash-oil 13%. This investigator has carried out extensive tests in order to determine the effect of "stripping" on the quality of gas. With a plant dealing with 100,000 cubic feet of coal-gas per day, he obtained data showing a loss of 63% of the candle-power (Met. No. 2 burner) and 6·2% of the calorific power (B.Th.U. gross), whilst the naphthalene decreased 80%, and the carbon bisulphide 50%

Willian[29] has also investigated the effects produced by "stripping" carburetted water-gas, but the effectiveness of such a procedure depends entirely upon the quantity of oil which is employed in the carburation of the gas. The temperature prevailing in the carburettor influences the result. Temperatures between 700° and 760° C. appear to produce the maximum amount of toluene. Higher temperatures will tend to increase the benzene, while lower temperatures produce paraffins and olefines which, as is well known, are objectionable to explosives manufacturers owing to their forming a sludge in the nitration process which is difficult to remove. The recovery of light oils from water-gas in this country, though attempted in the early days of the war, has not been followed up, partly owing to the paraffins present in the recovered spirit, and also on account of the attenuated nature of the carburetted water-gas which has resulted from the shortage of gas-oil. Willian's figures show that, with thorough scrubbing, the crude spirit recovered from carburetted water-gas amounts to about 10% of the oil used, and consists of benzol 35%, toluol 25%, solvent naphtha 10%, heavy naphtha and wash-oil 30%. The loss of candle-power due to scrubbing was 50·8%, and of calorific value 4·2%.

H. S. and M. D. Davis[30] have pointed to the fact that if the aim of washing the gas is to extract toluene only, then much less oil need be used for washing. Only one-third as much oil is theoretically necessary to absorb completely all the toluene as to absorb completely all the benzene.

T. H. Butler and F. J. W. Popham[31] in a valuable paper on the fractional separation of benzene, toluene, and xylene, have shown that during rectification the loss on washing of the crude spirit is a very serious item in the cost of manufacture, and it may amount in some cases to 10%. A crude benzol obtained from coal-gas shows a very much higher loss on washing than one from coal-tar. The differences in the working of paraffinoid crude benzols and those free from paraffins are discussed, and it is to be noted that difficulties, when paraffins are present, are observed in the fractionation owing to the absence of clear "cuts." This involves the rejection of a large proportion of the distillate, even though the paraffin content may be as low as 0·5%. Another objection is the formation of a deposit on the coil in the still which reduces the heating capacity to a detrimental degree.

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[29] *Loc. cit.*

[30] *J. Ind. and Eng. Chem.*, 1918, 10, 712.

[31] *J.*, 1918, 221 T.

Characteristics of Coke.

There is a well-defined distinction between coke obtained from horizontal retorts and that yielded by continuous "verticals." The former retorts yield a hard and lustrous product, whereas the coke from the latter is softer and more suitable for domestic use. J. Dickson [32] has given the following figures, which relate to the coke yielded by the same type of coal when carbonised in horizontal and vertical retorts respectively:

	Fixed carbon. %	Volatile matter. %	Ash. %	Sulphur. %	Water. %	Calorific power. Calorimeter. B Th U.	Calorific power. Calculated. per lb.
Horizontal .	75·55	0·73	6·09	1·44	16·19	13,300	13,100
Vertical . .	89·12	0·53	6·42	0·51	3·42	13,600	13,420

The above samples of coke were evidently well carbonized, for, normally, the volatile content rarely falls below 1·0%, and often exceeds 2%.

G. W. Hewson,[33] in dealing with the methods employed for testing the hardness of coke which is to be utilised for metallurgical purposes, suggests that a test as follows should be carried out. A weighed quantity of dried coke (sized between 1-inch and ½-inch mesh) is placed in a drum of 26 inches diameter together with a dozen cast-iron balls 1¼ inches in diameter, and the drum is rotated for one hour at a speed of about 13 r.p.m. The coke is then withdrawn, placed on a ½-inch sieve, and that which remains on the sieve is weighed and calculated as a percentage of the original weight. Hewson also indicates how a comparatively small variation in the proportion of ash in the coke may very easily render the iron produced relatively useless. He describes the method of calculating the amount of "available" carbon in coke, each 1% of ash requiring half its weight of carbon to melt the slag which it produces, and each 0·1% of sulphur requiring 0·8 of its weight of carbon.

The increased extent to which coke-breeze is being employed as a fuel has awakened consumers to the fact that, as yet, no definite standard has been established which covers the sizing of breeze. C. J. Bacon,[34] however, classifies breeze as that portion of the product which passes over a ½-inch screen and through a ¾-inch screen, the portion which passes through the ½-inch screen being called coke-dust. E. B. Elliott[35] has analysed two typical samples of breeze, and gives the following figures: Volatile matter, 4·1, 4·3%; fixed carbon, 74·1, 69·2%; ash, 21·8, 26·5%. He states, further, that the average sample of breeze has a calorific power lying between 10,000 and 11,000 B.Th.U. per lb., and is worth 60 to 80% of its weight in good, soft coal.

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[32] *Gas J.*, 1918, **144**, 188; *J.*, 1918, 680A.
[33] *J.*, 1918, 60T.

Considerable headway has been made with the employment of coke as a fuel for road vehicles. Clarkson[36] has introduced, for use on the omnibuses of the National Steam Car Company, an annular boiler operating at a steam pressure of 300–350 lb. per square inch. On the road, the standard 3-ton vehicle will run a mile on a consumption of 5 lb. of coke when fully loaded. At prevailing rates this amounts to a fuel charge of 1*d.* per mile.

"*Direct*" *Ammonia Recovery.*

It is interesting to note that whereas, in pre-war days, nearly the whole of the ammonia produced from coal was recovered in the form of ammonium sulphate, the exigencies of the present situation have been responsible for a change from the production of this salt to the preparation of concentrated ammoniacal liquor, a process which has continued to extend, so that the annual output[37] now amounts to 70,987 tons out of a total recovery for the United Kingdom of 433,703 tons of ammonia. The latest figures now available clearly indicate that the production of ammonia is on the increase, for in 1916 the aggregate output exceeded that of 1915 by more than 7,000 tons, in spite of the fact that gasworks as a whole produced 1,400 tons less, probably owing to a decrease in the quantity of coal they carbonised. It is possible, moreover, that the working loss suffered in gasworks is tending slightly to increase, owing to the fact that in this respect the manufacture of concentrated ammonia is liable to be followed by greater waste than is the case with the ordinary process of sulphate making. The increase in the aggregate output, in fact, is entirely due to more effective recovery at coke-oven establishments, where an additional quantity of 14,000 tons was produced.

In the early days of its inception the 'direct' process was responsible,

[34] *Proc. Illinois Gas Association,* Mar. 21, 1912.

[35] *Gen. Electric Review,* 1918, **21**, 476.

[36] *Tramway and Railway World,* xliv., 1918, **44**, 115.

[37] *Gas J.,* 1918, **143**, 62.

in some instances, for a very low efficiency of recovery. In fact, in place of the 25–30 lb. of ammonium sulphate per ton of coal which was anticipated when the process was first adopted some seven years ago, the recovery barely exceeded 15–20 lb., and not only was the yield of the ammonia poor, but the whole system of gas purification was found to be subject to mysterious and anomalous periods of disorganisation. It was found, in general, that such disorganisation was most frequent when the oxide of iron purification material was highly charged with moisture. At such times it was apt to " sour " in the purifiers, and the by-passing of a large amount of ammonia frequently failed to activate the sluggish material.

The Chief Inspector under the Alkali Acts [38] has suggested that, in order that derangement may be avoided, it is necessary that the moisture content of the oxide should be carefully regulated, that a supplementary ammonia washer should be introduced just prior to the purifiers, and that other steps should be taken in order to maintain as far as possible an equable temperature in the dry-purification vessels. During 1917 an opportunity was found to test the value of these suggestions, and it is gratifying to learn that already some substantial advance has been made towards scientific control. Although the elucidation of the problem is by no means complete, and further research remains to be done, the effect of the disorganising factors has been satisfactorily determined, and the ammonia recovery figure has shown improvement. Any advance in the development of this process will be eagerly followed, for, from the gas-engineer's point of view, its introduction means some considerable saving in the cost of recovering ammonia.

W. S. Curphey [39] has given some interesting information with regard to the ammonia (commonly called " virgin liquor ") which is derived from the condensible products of coal, and that which is found in the crude gas, and which is eventually removed in the ordinary wet-purification plant, or, in the " direct " process, by passage through an acid-bubbler. Results previously recorded indicated that about 42% of the total ammonia was found in the virgin liquor, but it is now shown that the figure is at least 50%, and probably, 60%. This fact may to some extent be responsible for the heavy loss of ammonia in the distillation of the condensed liquor, a loss which at one works reached a figure equivalent to 5½ lb. of sulphate of ammonia per ton of coal, or 20% of the total amount recoverable. Of the ammonia thus lost in the effluent liquor, from 83 to 99% was of the " fixed " variety, clearly indicating that an insufficiency of lime was being employed in the liming stills.

[38] *Alkali Works Report*, 1917, 53 ; *J.*, 1918, 498A.

[39] *Loc. cit.*

Purification.

During the past few years there has been a growing tendency to regard a small quantity of ammonia as having a beneficial influence on the process of oxide purification. The action of the ammonia is not perfectly clear, but it cannot be (as so frequently stated) that it combines direct with the hydrocyanic acid and free sulphur to form ammonium thiocyanate, for the amount of ammonia required[40] would be greatly in excess of that actually present in the gas at this period. Prussian blue, however, is the bug-bear to be avoided, and it is well known that the formation of this salt cannot take place when alkaline conditions prevail. When lime is employed in lieu of ammonia, the desired condition of alkalinity is not maintained, owing to the lime being quickly carbonated by the carbon dioxide coming forward with the gas, although carbonates are effective in alleviating trouble from the formation of ferric sulphate.

Curphey[41] has directed special attention to the determination of the minimum amount of ammonia which is necessary, in his opinion, to maintain the purifiers at maximum efficiency. Results as yet are difficult to interpret, but there is reason to believe that the amount of ammonia required bears a direct relationship to the quantity of ferrous sulphate formed, and that the formation of ferrous sulphate is favoured by excessive moisture and possibly by low temperature. Ferrous sulphate is an objectionable constituent in that it will not undergo revivification, or at least only in the presence of alkalis or carbonates in the mass, and then only slowly. Moreover, it reduces the rate of revivification of the whole material, and may give rise to the well-known effect of "souring" of the oxide. The quantity of ferrous sulphate actually present at any given moment appears to be small, probably only a fraction of 1% in normal working, but in relation to the actual reacting weights of hydrogen sulphide and ferric hydroxide this quantity cannot be regarded as negligible. This is owing to the fact that it is the surfaces of the oxide particles which react, and if the particles are coated with a skin of ferrous sulphate the activity of the mass may be immensely reduced. Curphey makes a suggestion with regard to the point of admission of the ammonia to the purifiers which merits attention. In ordinary practice it is customary to admit all the ammonia with the crude gas entering the first purifying vessel. It is now suggested, however, that a certain proportion of the ammonia should be introduced at the second vessel as well, instead of supplying an excess to the first box in the hope that some of it may escape absorption and travel further along the series.

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[40] "*Modern Gasworks Practice*," 370.

[41] *Alkali Works Report*, 1917 53.

H. W. Hemingway[42] has introduced a process for the elimination of hydrogen sulphide from gases by treating them in purifiers with iron carbonate, and he extends the process to the treatment of ammoniacal liquors. The process is carried out in such a manner that the ferrous carbonate is recovered for further use. When applied to the desulphurisation of coal-gas, the gas is passed through scrubbers in the usual manner, and ammoniacal liquor derived therefrom is conveyed to a tank and there treated with ferrous carbonate, The liquor having thus become "sweetened," and the iron salt having subsided in the form of sulphide, the sweet liquor (ammoniacal liquor deprived of its hydrogen sulphide) is run off to a still, or returned to the scrubbers, while the iron sulphide precipitate is converted into ferrous sulphate for use in the next stage of the process. The sweet liquor is conveyed to a second tank, and is there treated with the ferrous sulphate before referred to. The ferrous salt, absorbing carbonic acid, subsides as ferrous carbonate, and the sweet liquor (now containing a little extra ammonium sulphate) is run off to a still, while the ferrous carbonate precipitate is withdrawn for re-use in the first stage of the process. The ammoniacal liquor, draining from the precipitate, is led to the ammonia still as before. By the third stage of the process, ferrous carbonate is reproduced for use in the first stage, and the cycle of operations may be repeated without the introduction of further supplies of the ferrous salt, except so far as may be necessary for making good trifling losses in working.

The Feld process for the simultaneous recovery of ammonium sulphate and purification of coal-gas has been employed in Germany to some extent, and in isolated instances it was introduced into this country just prior to the war. The original process has, however, been since modified, and, according to Sander,[43] it now takes the following form. The crude coal-gas is washed with a solution of ammonium tetrathionate, the reactions occurring being on the following lines:

$$(a)\quad 6NH_4OH + 4(NH_4)_2S_4O_6 = 5(NH_4)_2S_2O_3 + 2(NH_4)_2S_3O_6 + 3H_2O.$$

$$(b)\quad 3H_2S + (NH_4)_2S_4O_6 = (NH_4)_2S_2O_3 + 5S + 3H_2O.$$

The tetrathionate lye which has been employed for washing is then treated with a current of sulphur dioxide. In this way the ammonium thiosulphate and trithionate formed are reconverted into tetrathionate:

$$(c)\quad 2(NH_4)_2S_2O_3 + (NH_4)_2S_3O_6 + 2S + 3SO_2 = 3(NH_4)_2S_4O_6.$$

When the tetrathionate lye becomes sufficiently concentrated it is heated, decomposition taking place with the formation of ammonium sulphate, free sulphur, and sulphur dioxide:

$$(d)\quad (NH_4)_2S_4O_6 = (NH_4)_2SO_4 + 2S + SO_2.$$

[42] Eng. Pat. 117387; *J.*, 1918, 500A.

[43] *Chem.-Zeit.*, 1917.

The sulphur dioxide and a portion of the free sulphur are then used again in the earlier stages of the process. With German gas-coal it has been found that sulphur exists in excess of that required for the formation of the sulphate of ammonia; thus, some considerable quantity of free sulphur also results as a by-product.

Tar Fog.

The estimation of tar fog in coal-gas has always presented difficulties, but as processes such as the "direct" recovery of ammonia or complete purification by means of liquor, become more common, so does the necessity for the removal of tarry vesicles assume greater importance. A. Edwards[44] has given details of a method for the estimation of tar in which the gas is filtered through a disc of filter paper cut to a diameter of 1·8 cm. and exposing 2 sq. cm. of filtering area. The volume of gas which has to be passed through the filter paper to give a stain within measurable limits varies from 80 to 9000 c.c., according to the proportion of tar fog present. The method employed is a visual one, which has been made quantitative as well as comparative. If the area of the stain (A) on the filter paper is known, also its density (D), the weight of the tar to give unit density on unit area (T), and the volume of the gas (V), then the quantity of tar fog present in the gas is ADT ÷ V, and this may be expressed in grains per cubic foot or grams per cubic metre, according to the particular units taken. Edwards has carried out tests in this manner, and has given the following interesting figures showing the amount of tar (in grains per cubic foot) at the outlet of various points in the manufacturing plant employed for coal-gas: (*a*) Condensers (hydraulic main employed), 30; (*b*) Condensers (partly hydraulic, partly dry mains), 15; (*c*) P. & A. Extractor, following (*a*), 0·25; (*d*) Rotary exhausters (following dry mains and condensers), 8; (*e*) Livesey washers, following (*d*), 0·60; (*f*) Washer-scrubbers, following (*e*), 0·40.

Cyanogen.

The importance of cyanide as a war product has led to an extension in the number of works at which it is recovered from the gas. Cyanides are obtained from coal-gas in two forms, *i.e.* sodium ferrocyanide, or ammonium thiocyanate, according to the process employed, but the simplicity of the Williams polysulphide method[45] has commended it to the most general adoption, even though it recovers the product as a thiocyanate, whereas from the commercial standpoint, the ferrocyanide is, perhaps, to be preferred. The advantages of obtaining a ferrocyanide direct, however, are not commensurate with ease and regularity of operation which the Williams process offers. Butterfield[46] has stated that German gasworks alone have yielded in recent years approximately 10,000 tons of ferrocyanide per annum, while the output of the British gasworks has not exceeded 5,000 tons. Were cyanogen recovery to be extended to all gasworks in this country, the annual output would amount to 24,000 tons of ferrocyanide or the equivalent in other cyanide products. Apart from any profit attached to the process (and there is no margin for extravagance in working expenses), it may be said that the removal of the hydrocyanic acid from the gas is followed by many indirect advantages not actually to be measured in terms of money, for the product is responsible for derangements in dry purification,[47] and for the corrosion of steelwork, more particularly gasholder sheeting.

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[44] *J.*, 1918, 35T.

[45] Williams, "*Modern Gasworks Practice,*" 372.

The Bartlett Hayward Company in America has recently introduced a cyanide recovery process[48] which is based on the well-known Bueb method. The crude gas, completely freed from tar, is washed with a 25–30% solution of ferrous sulphate, 3·565 lb. of ferrous sulphate being required per pound of cyanogen removed. Ammonium sulphate and ferrous sulphide are formed. The latter is then used for further washing the gas, when the cyanogen is extracted as $(NH_4)_2Fe_2(CN)_6$, which reacts with the hydrogen sulphide and ammonia in the gas, producing some ammonium ferrocyanide and ferrous sulphide. This liquor is then pumped through a still on its way to the neutralising tank, where some of the ammonium ferrocyanide is again converted into the double salt, which passes into the neutralising tank, while the ammonium sulphide is condensed and run into the precipitating tank. A small quantity of sulphuric acid is added to the sludge in this vessel in order to neutralise it. The end product from this reaction is an insoluble double ferrocyanide of iron and ammonia, with a solution of ammonium sulphate, while the hydrogen sulphide liberated is taken to purifiers or burned.

Naphthalene.

It is a somewhat remarkable fact that in the earlier period of the war, when the "C" process of tar-washing was introduced, there was in

[46] *Gas World*, 1918, **62**, 463.

[47] *Ante*, *ref*. 28.

[48] *Gas World, Coking Supplement*, February 3, 1917, 20.

many instances a marked tendency for naphthalene troubles to increase. This may be explained by the fact that the removal of benzene and its homologues from the gas deprived the latter of constituents which have a solvent action on naphthalene, while at the same time the very fact that gas and tar came into intimate contact set up conditions which were favourable for an exchange of naphthalene from tar to gas. The recognised oil-washing process has been followed by variable results in the same direction, but so long as the correct grade of washing oil is employed with intelligence there is no reason why it should not be instrumental in reducing the naphthalene, as shown by Willian's results already quoted.[49] Many benzol plants are now fitted with a primary or vapour condenser, through which the hot still-vapours pass in counter-current to the benzolised washing-oil. If an outlet is provided at the base of this primary condenser, and the high-boiling condensates are run off to a separator tank, it will be found that they consist essentially of water, naphthalene, and naphthas. The water and naphthalene may be separated direct, or, to carry the process a stage further, it is profitable to erect a small secondary still in which the naphtha portion may be dealt with. If the distillate is collected, cooled, and run to a shallow settling-tank, the remainder of the naphthalene may be recovered, while the liquid portion will consist largely of naphtha, which may be sold direct as such or returned to the debenzolised oil-tank. Such a process forms, in the writer's opinion, the nucleus of what may become a recognised method for naphthalene removal and recovery in the future, and in some respects it bears a similarity to the highly effective system of anthracene oil-washing[50] which has been adopted throughout the works of the South Metropolitan Gas Company.

The inability of gas to hold anything more than a very small quantity of naphthalene at low temperatures has been illustrated by one or two workers, and from a scientific point of view it is a little disappointing that the results of research do not agree more closely. For instance, if a curve be plotted from a series of Butterfield's results,[51] it is seen that, in cooling gas from 68° to 50° F., 10 lb. of naphthalene will be deposited per million cubic feet, whereas, from the results obtained by J. S. G. Thomas,[52] the amount deposited over the same temperature range is shown as nearly 15 lb. Both workers agree, however, that at 32° F. the saturation of the gas can be no more than about 2·5 lb. of naphthalene per million cubic feet.

So far as the formation of naphthalene during carbonisation is concerned, T. D. Miller[53] has stated that the compound is formed from the gas and not from the coal direct, though in his opinion the greater proportion is derived from the aromatic hydrocarbons, and it seems that the higher the percentage of carbon in the compound, the greater is its tendency to form naphthalene.

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[49] *Ante, ref.* 22.

[50] "*Modern Gasworks Practice,*" 302.

[51] *Inst. Chem., Special Lectures,* 1913, 46.

[52] *J.,* 1915, 701.

Analysis and Tests.

H. M. Russell[54] has suggested the following as a method of determining the quantity of sulphur in gas-oil: A mixture of 10 c.c. of the oil, 10 grms. of magnesium oxide, and 5 grms. of anhydrous sodium carbonate is heated gently in a 75 c.c. crucible for two hours and then raised to a white heat. When cool, the residue is boiled with 50 c.c. of water, 2 c.c. of bromine water added, and boiled for five minutes. The liquid is poured off and the treatment repeated with 30 c.c. of water. The solutions obtained are filtered and acidified, and precipitated by barium chloride solution.

Since benzol recovery from coal-gas became general, a number of methods have been suggested and adopted for the evaluation of the crude spirit. The lack of any definite standard test has, accordingly, led to a certain amount of confusion. For this reason reference may be made to the method of analysis which Adam[55] has introduced in connection with the large quantity of crude spirit which is handled by the Gas Light and Coke Company. The original paper must be consulted for details of the procedure recommended.

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[53] *American Gas Inst. News*, Sept. 1917; *J.*, 1917, 1229.

[54] "*The Operation of Gas Works*," 1917.

[55] *Gas J.*, 1918, **141**, 65; *J.*, 1918, 50A.

MINERAL OILS.

By Arnold Philip,
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Chemical Analysis of Petroleum and its Products.

The problem of the determination of the proportions of paraffins, olefines, aromatic hydrocarbons, and naphthenes in motor spirit, and also in all classes of petroleum oils, is of very great importance. This has been attacked with greater or less success by means of fractional distillation combined with fractional solution in liquid sulphurous acid by Edeleanu's method,[1] and by S. E. Bowrey's modification of Edeleanu's method at lower temperatures,[2] whilst F. M. Perkin is at present investigating Valenta's proposal for the use of dimethyl sulphate as a fractional solvent for aromatic compounds and olefines.[3]

A further important paper on Edeleanu's method of separation as used for motor spirit and kerosene has recently been published by R. J. Moore, J. C. Morrell, and G. Egloff.[4]

These authors use liquid sulphurous acid at temperatures of — 10° C. and — 18° C. for treating known binary and ternary mixtures of pure toluene, benzene, *p*-xylene, mesitylene, hexylene, octylene, cyclohexane, and other pure naphthenes, with pure light paraffins. They find that, provided the liquid sulphur dioxide used forms a sufficiently large proportion of the whole mixture, and the hydrocarbons in the mixture from which it is desired to separate one or more of them are also within certain specified limiting proportions, very good results can be obtained. Contrary to the previously accepted view, they also find that naphthenes of low boiling-point can be completely separated from paraffins of low boiling-point if a sufficiently large volume of sulphur dioxide is used.

[1] *Bull. A.I.M.E.*, 1914, **93**, 2313.
[2] *J. Inst. Pet. Tech.*, 1917, **3**, 287; *J.*, 1918, **455A**.
[3] *J. Inst. Pet. Tech.*, 1917, **3**, 311.
[4] *Met. and Chem. Eng.*, 1918, **18**, 396; *J.*, 1918, **329A**.

It is worthy of note that in all these mixtures it is the denser constituent which is preferentially soluble in the sulphurous acid.

E. W. Dean and H. H. Hill[5] have investigated various methods for determining the amounts of unsaturated hydrocarbons in gasolenes by means of the sulphuric acid absorption method, and they have also determined the iodine and bromine values and the specific temperature rise (Maumenés' test) for a series of commercial gasolenes. They consider Maumené's heat test to be useless for these materials on account of the uncertainty introduced by the latent heat of vaporisation of the spirit which is accidentally evaporated. They also find that for the particular gasolenes examined (22 in number), the ratios of the iodine values (varying from 47 to 293) to the sulphuric acid absorption percentages (varying from 8 to 46) are constant or nearly so between the values of 5·3 and 7·5. In the experience of the present writer this is not even approximately true for motor spirits consisting of mixtures of paraffins, cracked spirits, benzol, &c., and if it were true it would clearly not be necessary to make both of these determinations. The publication of iodine values and sulphuric acid absorption figures, together, perhaps, with the bromine values and Maumené specific temperature rises of a large number of different cracked spirits of known origin and blends of such with petrol from different known sources, would probably be of value in enabling a conclusion as to the character of a given spirit to be rapidly arrived at. Although such tests are arbitrary, yet if they yield concordant results they may be of great use for technical purposes. It is to be hoped that results of tests of this character may be forthcoming at an early date.

The paper by B. T. Brooks and I. Humphrey[6] on the action of concentrated sulphuric acid on olefines, with particular reference to the refining of petroleum distillates, is of remarkable technical interest. No experimental investigation has previously been made upon the action of strong sulphuric acid upon any pure olefines except ethylene, propylene, butylene, and the amylenes. The usually accepted view is that when petroleum oil is refined by treatment with sulphuric acid, the olefines present are polymerised to tars and are completely removed with the acid sludge. The authors, however, find that on treating pure olefines (up to $C_{16}H_{32}$) with sulphuric acid (sp. gr. 1·84) at 15° C. the following compounds are formed: (1) polymers of the olefines; (2) the corresponding secondary and tertiary carbinols; (3) acid alkyl sulphates; (4) neutral alkyl sulphates; (5) probably additive molecular compounds of the olefines or of their isomers with sulphuric acid. The proportions in which these compounds are formed depend upon:

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[5] *U.S. Bureau of Mines Tech. Paper*, 181; *J.*, 1918, 402A.

[6] *J. Amer. Chem. Soc.*, 1918, 40, 822; *J.*, 1918, 361A.

(*a*) The nature of the olefines: the tendency to form alkyl sulphates and carbinols decreases whilst the tendency to form olefine polymers increases with the molecular weight of the olefine treated, above that of the amylenes and hexenes, for which hydrocarbons the tendency to form alkyl sulphates and carbinols is a maximum and the tendency to form polymers is a minimum.

(*b*) The relative volumes of the acid and the olefine: the smaller the volume of acid used in refining, the larger is the proportion of neutral alkyl sulphate appearing in the residual treated (refined) olefine.

(*c*) The strength of the acid: when 100% acid is used no carbinols are formed, whilst 94% acid yields less carbinol than 85% acid. The formation of the carbinols by the action of 85% acid is direct, that is to say, it is not due to a preliminary formation of acid esters from which the carbinols are subsequently formed by hydrolysis.

(*d*) The temperature at which the reaction takes place: this should be kept at about 15° C. At 0° C. the action is very slow, and at temperatures much above 15° C. it is difficult to control.

(*e*) The time of contact of acid and olefines: if the time is prolonged there is an increased formation of polymers at the expense of the carbinols. This statement of the authors appears to suggest that the polymerisation of the olefine may occur *via* the carbinols formed, or that at least the carbinols may have some part in the mechanism of the olefine polymerisation.

No tars are formed by the treatment of any pure olefines with any sulphuric acid up to 100% acid at 15° C. The polymers of the olefines are frequently dipolymers, and in all cases still contain at least one double bond and therefore possess marked iodine values. The polymerisation does not in fact result in the formation of naphthenes. The polymers are all much more stable as regards the action of strong sulphuric acid than are the original olefines from which they are formed.

Chemically pure lower homologues of the olefine series dissolve completely in sulphuric acid of sp. gr. 1·84 at a temperature below 20° C., forming clear, nearly colourless solutions from which, when diluted with water, the carbinols mixed with some of the original olefines or their isomers or polymers separate as an oily layer. Similar treatment of chemically pure higher homologues of the olefine series on the other hand results in the formation of two layers—an upper oily, and a lower acid layer. The oily layer, when washed with water and then with aqueous caustic soda solution and dried, has a higher sp. gr. than the parent olefine from which it was formed, and yields on distillation a considerable fraction of higher boiling-point than the original olefine, owing to the formation of the polymerised olefines.

Saturated hydrocarbons and aromatic hydrocarbons are not acted upon by sulphuric acid of sp. gr. 1·84 at any temperature below 25° C., but when fuming acid is used, both classes of hydrocarbons may be readily sulphonated.

It should, however, be added that the statement that aromatic hydrocarbons are not acted upon at all by sulphuric acid of sp. gr. 1·84 appears to have been contested by F. B. Thole in a paper on the estimation of benzene and toluene in petroleum (*J.*, 1919, 39T).

Refining Motor Spirits and Kerosenes.

If the refining by means of strong sulphuric acid of motor spirits or kerosenes containing olefines is considered in the light of the above results, it is clear that those grades which are completely soluble in sulphuric acid at ordinary temperatures must consist practically entirely of the lower members of the olefine series, whilst other grades which yield oily layers insoluble in the acid do so either because the acid treatment is not carried sufficiently far, or because the spirit or kerosene contains a certain proportion of higher homologues of the olefine series, paraffins, naphthenes, or aromatic compounds. In such cases if olefines were present in the original oil, the residual oily layer always possesses an increased specific gravity and distillation temperature. But it is observed that the refined oils obtained by treating spirits or kerosenes with liquid sulphurous acid always possess lower specific gravities than the original unrefined oils from which they are derived. When refining by means of sulphuric acid, therefore, two separate actions take place concurrently; firstly, the partial removal of the olefines from the spirits or kerosenes, thus tending to lower the gravities of the residual oils; and secondly, the polymerisation of some of the olefines and the formation of neutral alkyl esters, both of which products pass into the refined oils, tending to raise both their gravities and their distillation points. The net result is that a rise of the specific gravity and of the distillation temperature takes place.

The analytical determination of the amount of olefines present in motor spirits and kerosenes by treatment with strong sulphuric acid is therefore not a quantitative operation, but may and does nevertheless possess a considerable technical value as an arbitrary test to assist in forming a judgment as to their origin. A closer approximation to the determination of the olefines in such hydrocarbons by treatment with sulphuric acid than is possible by the method ordinarily used, is to agitate the oil thoroughly with cold acid, separate the acid layer, wash the oily layer with water and then with an aqueous caustic soda solution and with water again, then dry the oil and distil up to the highest temperature at which the original oil distilled before treatment: any residue then remaining in the flask clearly consists either of poly merised olefines or of neutral alkyl sulphates or both, and its volume should be added to the other loss observed on treating the original oil with sulphuric acid.

The neutral alkyl sulphates left in motor spirit after refining with sulphuric acid are considered to be one of the causes of the instability sometimes noticed in these products. The neutral esters rapidly decompose at 140° C. or higher temperatures, but decomposition also takes place slowly at ordinary temperatures, and causes the darkening of the oils on standing and the separation of a small proportion of a brown viscous layer containing a little free acid and much resinous matter. Spirit and kerosene refined with sulphuric acid should therefore always be subsequently redistilled.

Diolefines are considered to be sometimes present in spirits and kerosenes, especially those which have been obtained by cracking heavier oils at unusually high temperatures, such as 600° to 800° C. It is the presence of these diolefines which chiefly gives rise to the troublesome "gumming" from resin formation sometimes observed. The authors, moreover, consider that it is the diolefines which, in contradistinction to the olefines, give rise to tar formation when treated with sulphuric acid. They further point out that it is desirable that the old sulphuric acid refining process for kerosenes and spirits should be discontinued or modified

Refining methods based on the use of fullers' earth or the action of such mild polymerising agents as the chlorides and sulphates of some of the heavy metals have recently been proposed.[7] If the method of refining with sulphuric acid is used, the authors find that treatment with about 6% by weight of 85–90 % acid, followed by washing with alkali in the usual manner and then by redistillation, gives a very sweet and stable product

Refining Lubricating Oils.

With regard to the refining of lubricating oils with sulphuric acid the authors point out that the very considerable iodine values of the refined oils appear to indicate that relatively large percentages of un-

[7] *Allgem. Ges. für Chem. Ind. m.b.H.*, Eng. Pat. 3572, 1914; *J.*, 1915, 1094.

saturated hydrocarbons, probably polymerised olefines, possessing only one double bond, are present. The iodine value which the authors quote for refined lubricating oils is 12. Out of hundreds of refined mineral lubricating oils examined by the present writer, a lower value than 11·5 has never been observed, and it is usually from 14 to 16, and sometimes as high as 21—all as measured by Wijs' method. The tars, which are invariably obtained when crude lubricating oils are refined with sulphuric acid, are considered not to be due to the presence of simple olefines, but are probably formed from diolefines, or perhaps other substances; but our knowledge of the real nature of the hydrocarbons, nitrogen bases, naphthenic acids, sulphur compounds, &c., occurring in crude lubricating oil distillates, is so extremely meagre that nothing positive can be said as to the nature of the tars formed.

No reference to the alteration of gravity of lubricating oils before and after treatment with sulphuric acid is made in this paper, but it is interesting to note that Dunstan and Thole[8] observed in six cases that the density of the refined oil was less than that of the original oil. This is also stated to be in accordance with the observation of J. Marcusson;[9] it is, however, the reverse of the change in density which is observed on treating spirit and kerosene with sulphuric acid. This may be due to the more complex nature of the lubricating oils as compared with kerosene and spirit referred to above. With regard to the viscosity changes produced on treating lubricating oils, Brooks and Humphrey remark that so far as the action of sulphuric acid on olefines is concerned, the refined oils should show greater viscosities than the original distillates, but that this difference is usually more than counterbalanced by the removal of other substances, in some cases asphaltic material.

The naphthenic acids separated from Texas oils are heavy, viscous, and nearly odourless oils, and are therefore superior for many industrial applications in the form of soaps to the naphthenic acids obtained from Russian and also Mexican oils, which possess strong and disagreeable odours.

The Viscosity of Oils.

An interesting paper on the relation between the viscosity and the chemical constitution of lubricating oils has been published by A. E. Dunstan and F. B. Thole.[10] All the tests were carried out on six oils both before and after refining with two volumes of concentrated sulphuric acid. In three cases the refining losses were 33·3%, 20%, and 50% respectively: these figures appear to indicate a somewhat drastic treatment.

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[8] *J. Inst. Pet. Tech.*, 1918, **4**, 191; *J.*, 1918, 291A.

[9] *Chem.-Zeit.*, 1913, **37**, 533.

[10] *J. Inst. Pet. Tech.*, 1918, **4**, 191; *J.*, 1918, 291A.

In every case the refined oils possessed lower viscosities and densities but higher molecular weights than the corresponding unrefined oils, but the coefficients of alteration of viscosity with temperature remained practically unchanged. As a rule, the ratio of the percentage of carbon to hydrogen was also lower in the refined oils. One Russian lubricating oil was, however, an exception to this rule.

Although this paper is nominally chiefly concerned with the viscosities of lubricating oils, it actually deals very largely with the consideration of their "lubricating values." The authors seem to consider that there is at present no method of determining the lubricating value of an oil, but in spite of this, throughout the paper they frequently make statements showing that one oil is a better or a worse lubricant than another. It is clear that such statements must be based upon the results of some measurements, and these measurements are presumably either the somewhat vague results of practical experience with machinery under running conditions, or have been obtained from tests made on some type of mechanical oil tester.

The present writer's experience on this subject has been that when the results of the lubricating values of a large number of oils of the same class, as measured on a Thurston oil tester at the same temperature, bearing pressure, and speed of rubbing surfaces, by an observer ignorant of the viscosities of the oils, are tabulated in their order of magnitude, they are found to have been arranged in the reverse order of the viscosities of the same oils at the same testing temperature. This experience is in accord with the authors' statement that for lubricants the lowest viscosity compatible with circumstances is essential, because otherwise energy is absorbed needlessly and converted into heat. The lubricant is concerned with the transformation of solid into liquid friction, and therefore its own internal friction must be as near zero as possible.

In the writer's opinion we do at the present time possess a measure of the lubricating value of an oil in the results of tests in a mechanical tester such as that of Thurston. As to how far these results are accurately directly proportional to the real lubricating values is perhaps not fully demonstrated, but the results obtained are of real value, and it is difficult to understand how it is otherwise possible to know that one oil is or is not a better lubricant than another. This knowledge is, however, assumed by engineers and chemists and is certainly tacitly assumed by the authors of this paper.

A modified mercurial viscometer for determining the viscosities of volatile liquids is described by F. M. Lidstone,[11] whilst a paper on Dubrisay's method of testing the viscosity of lubricating oils has been published by P. Nicolardot and P. J. Masson,[12] and a patent has been granted for an unusual method of determining the viscosity of fluids to A. G. M. Michell.[13]

The Standardisation of Distillation Tests for Motor Spirit.

The multiplicity of methods which have been proposed for testing motor spirit by distillation leads generally to much difficulty and inconvenience when it is desired to compare the figures of tests made on spirits from the same or different sources which have been reported upon by different analysts. It is not of much importance whether a given method of distillation test gives rather lower or higher values from any given fraction. What is of the greatest importance, however, is that the method used shall be capable of giving as closely concordant results as possible on repeat tests when made by the same or different observers. The method should also be as rapid, simple, and easy to carry out as the nature of such a test permits.

In 1904 H. S. Garry and H. J. Watson[14] called attention to the necessity for a standardised test for petroleum spirits similar to that adopted for benzol. This standardisation has not so far been achieved, but has recently been again strongly advocated by A. Duckham[15] and other prominent members of the Institution of Petroleum Technologists, and it is hoped that action will shortly be taken in order to decide upon a generally acceptable method of test. It is not necessary that the selected method shall embody all the details of any test now in use. It may and probably will be finally arrived at by a judicious selection and combination of details of any or all of these processes. It is somewhat remarkable that of two of the most recent and important papers on methods of testing petrol by fractionation,[16] neither gives the results of a series of repeat tests on one sample of spirit. Such a series of tests is always necessary in order to exhibit the variations in the results, which are to be expected from experimental errors inherent in any particular method.

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[11] *J.*, 1918, 148T.

[12] *Ann. Falsif.*, 1918, **11**, 77 ; *J.*, 1918, 499A.

[13] Eng. Pat. 117234 ; *J.*, 1918, 533A.

[14] *J.*, 1904, 701.

[15] *J. Inst. Pet. Tech.*, 1917, **4**, 4

[16] E. L. Lomax, *J. Inst. Pet. Tech.*, 1917, **4**, 6 (*J.*, 1918, 116A), and N. A. Anfilogoff, *J.*, 1918, 21T.

Attention was called to this omission by Cadman in the course of the discussion on the paper by Lomax.[17] All the results of tests given were, it is true, the means of four or five separate tests, but the results of these separate tests were not stated.

Lomax states that the liability to personal error is much greater by the Engler method than by the Redwood, great care being required even by skilled manipulators to obtain concordant results on the same sample of spirit, while independent operators may obtain results varying within comparatively wide limits. The present writer fully concurs with this remark. His experience is that Engler's method is unworkable unless a very low standard of agreement of duplicate tests is to be accepted. In spite of this fact, which is probably also recognised by Anfilogoff, both these investigators have compared their methods with results of test obtained by the Engler method. This, no doubt, is only because this method possesses a long-standing and somewhat exaggerated text-book reputation.

A novel form of apparatus for fractionating petrol and other volatile liquids for laboratory testing purposes is described by E. Hildt.[18] It consists of a series of glass receivers each connected with its neighbour on its right and left by a tube at the top, and each heated to a fixed temperature higher than that of the next receiver. The spirit to be fractionated is admitted drop by drop into the receiver at the highest temperature. Here it is completely or partially vaporised, and the vapour flows along the tubes through the series of receivers until it arrives at one in which the temperature is sufficiently low for it to condense. This method of fractionation is so novel for laboratory testing that it will be of interest to have details of extended trials, especially as it appears to permit of a distillation curve being obtained at one operation over a considerable temperature range, the fractions being collected at any desired intervals.

A new form of fractionating column for laboratory use is described by H. F. Taylor.[19] It is built up in sections in a straight glass tube by means of pierced lead diaphragm discs, glass balls, and copper wire distance pieces: the results of practical trials of separations obtained by means of this apparatus with mixtures of (1) carbon bisulphide and benzene, (2) toluene and pyridine, and (3) alcohol and water show very satisfactory results as compared with the results of tests made on the same mixtures with eight different types of other well-known fractionating columns.

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[17] *J. Inst. Pet. Tech.*, 1917, 4, 34.

[18] *Comptes rend.*, 1917, 165, 790; *J.*, 1918, 26A.

[19] *J.*, 1918, 238R.

USE OF THE CALORIMETRIC BOMB IN ANALYSIS.

B. Blount[20] advocates the use of the calorimetric bomb for determining the calorific value of petrol as being preferable to methods involving the employment of modified forms of the Junkers calorimeter; in the latter devices the petrol does not always burn completely. In burning the petrol in the bomb he advises enclosing it in an envelope of combustible material of which the calorific value is known. Collodion is suitable for this purpose. The same author states[21] that a better method of determining sulphur in petrol than that of burning it in a lamp and absorbing the products of combustion is to burn it in a calorimeter bomb. Attempts to oxidise with nitric acid under a reflex condenser were not successful. The most dependable method is that of Carius.

The present writer's experience is that the determination of the calorific value, the sulphur contents, or the water formed by combustion of petrol and other volatile motor spirits can be more satisfactorily and safely carried out by other means than by the use of the calorimetric bomb. The combustion of as much as a gram of petrol is not safe when performed in the ordinary pattern bomb owing to the high temperature and pressure set up. Methods for the determination of the calorific value of sulphur and water formed by combustion, based on that described by W. Watson,[22] are much to be preferred. The small percentage of sulphur usually present in petrols can only be satisfactorily determined on fairly large quantities, much larger than can be used in any bomb combustion method.

B. Damour and M. de la Morinière[23] advocate the determination of total carbon in fuels generally by means of the bomb calorimeter. This method is applicable to oils and petrols, and the present writer has found it to be both rapid and accurate for this purpose for oils. Both hydrogen and carbon can be determined at the same time. The authors refer to the necessity for correction being made for the carbon dioxide remaining in the bomb; this is, however, not necessary if the bomb is fitted with both an inlet and outlet tube; for after the escape of the gases has reduced the internal pressure, a current of dry air can be passed through it whilst the bomb is warmed: this will remove the last traces of both carbon dioxide and moisture. The Mahler Kröcker bomb is fitted with double tubes which permit this operation to be carried out.

[20] *Analyst*, 1918, **43**, 89; *J.*, 1918, 200A.

[21] *Analyst*, 1918, **43**, 89; *J.* 1918, 200A.

[22] *J. Soc. Arts*, 1910, **58**, 990.

[23] *Rev. Mét.*, 1917, **14**, 789; *J.*, 1918, 143A.

Whether the bomb calorimeter is used for determining the calorific values of solid or liquid fuels, the results obtained are always the high values, and the low values can be only obtained by determining the amount of water present as such in the fuel, and also that of the water formed by the combustion of the fuel. Both of these amounts of water can be ascertained together if the bomb is fitted with the double tubes. Assuming that the hydrogen content of the ash and water-free combustible matter in a fuel is known, and if the water itself is determined, the low calorific value can be estimated more or less closely. This estimated correction can be applied to ordinary coals with a close approximation to accuracy, but it is not so close when applied to liquid fuels, and especially to those of the nature of motor spirit, owing to the greater variation of hydrogen in the latter class of fuel.

Unfortunately some difference of opinion appears to exist, as is shown in current technical literature, as to what the difference between the high and the low calorific value of a fuel should be understood to be. Some writers state that this difference is made up of two quantities: (*a*) the sum of the latent heat of vaporisation at 100° C. of the amount of water present in the fuel, together with that of the further amount of water which is formed by its combustion; (*b*) the heat given up by cooling this total weight of water from 100° C. down to some other temperature, usually 15·5° C. Other writers consider that the difference between the high and the low values should only consist of the latent heat of vaporisation of the water as given under (*a*) above, and it is with this latter view that the present writer strongly concurs. It is most desirable that uniformity of practice should obtain on this question. It is the low calorific value calculated on this second basis which is usually required for tracing the heat given off in the combustion of fuels under boilers or in internal combustion engines where the exhaust or flue gases escape at a temperature above 100° C. The heat, disappearing in the form of the latent heat of steam, cannot in fact be traced by direct temperature measurements. If it is generally accepted that the low calorific value of a fuel is its high value less the latent heat of vaporisation at 100° C. of all water present in it or formed by its combustion, and if both the low and the high values are stated, it is always possible by a simple calculation to obtain any other form of low value which may be desired for any particular purpose.

A portable apparatus for determining the amount of gasolene contained in natural gas by washing it out by means of high boiling-point oil is described by G. G. Oberfell,[24] whilst G. A. Burrell and J. W.

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[24] *J. Ind. Eng. Chem.*, 1918, 10, 212; *J.*, 1918, 231A.

Robertson [25] give results of tests made on natural gases to enable their compressibility to be calculated from the chemical analysis of the gas.

TRANSFORMER OILS.

The formation of "sludge" in the high resistance insulating mineral oils used in transformers and switches was first observed in about 1905. Since 1913 the Institution of Electrical Engineers has been carrying out an investigation of the subject, and it is now announced [26] that the report on the methods of testing transformer oils will shortly be completed.

The solid sludge formed in transformer oils is undoubtedly an oxidation product formed by the direct action of the air, often catalytically accentuated by the presence of metals and especially of copper. Possibly also ozone, formed by electric discharges from the transformers, plays a part, whilst oils containing large proportions of olefines and other unsaturated hydrocarbons are presumably more liable to sludge formation than oils which are free from these substances.

Recent experiments made by the present writer upon the question of sludge formation appear to show that the oxidation of petroleum oil, as used in highly insulated transformers by air at temperatures up to 100° C., is not of the nature of a substitution, but is chiefly an additive reaction, at least in so far as the hydrogen is concerned, for no water is formed, or if formed, it is only in very small quantities, very much less than is formed when coal is oxidised under similar conditions.

The formation of sludge in transformer oils, being due to the oxidation of the oil, is closely connected with the recent work which has been carried out upon the direct oxidation of paraffin wax by air. M. Bergmann [27] passed a fairly rapid stream of air through melted paraffin wax contained in an iron vessel at a temperature of 130°–135° C. for a period of from 15 to 18 days. The wax used was a white refined Galician wax of m. pt. 52° C. As to whether olefines were present in the wax is not known. The oxidation product obtained was a soft, brown, greasy mass possessing an acid reaction (the acid value was 132); on treatment with aqueous alkalis it formed a strongly lathering soap solution and was found to contain formic, acetic, normal butyric, and lignoceric acids and two other saturated acids, one of which is believed to be an iso-palmitic acid. A neutral crystalline substance, m. pt. 48° C., which was not a salt, was also separated. No details as to the yield of oxidised products are given. A patent describing the production of oxygenated and other compounds, including fatty acids, by blowing air or oxygen for a prolonged period through melted paraffin wax at 100°–120° C., has been granted to A. Schmidt.[28] When the colour of the product has reached deep yellow, about 70% of the wax has been converted into a mixture of fatty acids and small quantities of formaldehyde, alcohols, and the like. Mercuric oxide or paraffin wax which has already been subjected to the treatment may be used as a catalyst.

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[25] *U.S. Bureau of Mines, Tech. Paper* 158, 1917; *Petroleum Technology*, No. 32; *J.*, 1918, 199A.

[26] *J. Inst. E. E.*, 1918, 56, 334.

[27] *Z. angew. Chem.*, 1918, 31, 69; *J.*, 1918, 362A.

R. J. Moore and G. Egloff have published a paper on the preparation of fats and fatty acids from petroleum,[29] in which many references are given to patents for the chemical attack of petroleum oils by means of a preliminary formation of chlorinated compounds, which by suitable treatment can subsequently be converted into alcohols or acids. These authors are carrying out experiments on the effect of the silent high voltage electrical discharge field on mixtures of kerosene vapour with chlorine and carbon dioxide. In this connection attention may be called to L. B. Cherry's method of cracking petroleum oil vapours in a high-voltage high-frequency oscillatory electrical field (see p. 77) as offering a possibly simple and satisfactory method of causing combination to take place between petroleum vapour and chlorine.

The authors refer to Schmidt's work (*vide supra*) on the direct oxidation of paraffin wax by means of air and an almost identical process patented by Hulsberg and Seile[30] as being highly promising, and suggest the preliminary cracking of the paraffins of petroleum oil into olefines and the subsequent oxidation of these unsaturated and more readily oxidisable compounds.

Moore and Egloff remark that it is not improbable that Germany to-day is supplying a large part of her fats from synthetic production. It may be added that whether or not the economic production of food material from petroleum is already an accomplished fact, it cannot be denied that by the oxidation of petroleum, fatty acids can be formed, and that these can be transformed by known methods of hydrogenation or oxidation into the fatty acids which exist in natural fats and oils, and it is therefore not improbable that such petroleum products may, if they can be produced economically, at any rate be suitable for use for the manufacture of candles, soap, lubricating oils and painting oils, and thus liberate for food the natural fats and oils now used for these purposes.

[28] Eng. Pat. 109386; *J.*, 1917, 1090.

[29] *Met. and Chem. Eng.*, 1918, 18, 308; *J.*, 1918, 232A.

[30] Swiss Pat. 75653, 1917.

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[25] *U.S. Bureau of Mines, Tech. Paper* 158, 1917; *Petroleum Technology*, No. 32; *J.*, 1918, 199A.

[26] *J. Inst. E. E.*, 1918, 56, 334.

[27] *Z. angew. Chem.*, 1918, 31, 69; *J.*, 1918, 362A.

Cracking in the gaseous phase is a safer operation than is the carrying out of the operation on the liquid phase at the same temperature and pressure, since the pressure is more readily controlled, and if a breakdown occurs, the results are less serious from an escaping high-pressure gas or vapour than from a liquid escaping under the same conditions. If therefore cracking is carried out on oil in the liquid phase, the strength of the walls of the cracking chamber must be made amply sufficient by using greater thickness of metal, and the volume of the liquid oil must be kept small. On the other hand, trouble due to the separation of carbon during the cracking process is generally much more marked when the oil is cracked in the gaseous than in the liquid phase; the carbon separating on the walls of the cracking vessels (usually tubes) tends to block these up and also much reduces their thermal conductivity; this reduction of conductivity either decreases the output of cracked oil or necessitates an increased external furnace temperature, thus lowering the elastic limit of the steel and increasing fuel consumption. Moreover the carbon in contact with the heated steel is absorbed by a cementation action, thus tending to render the steel brittle.

In most modern cracking plants the operation is continuous—that is, the oil or oil vapour passes continuously through the cracking chamber.

L. B. Cherry[34] appears to have made a striking advance in the solution of the problem as to what is the best method of cracking kerosene oil. In his process a high-voltage high-frequency silent oscillatory electric current is passed through the vapour of the oil mixed with some gas containing hydrogen, such as methane (natural

[33] *J.*, 1917, 243.

[34] Amer. Electrochem. Soc., Oct. 3, 1917; *J.*, 1917, 1266. U.S. Pat. 1229886; J., 1917, 863.

gas), superheated steam, or hydrogen itself, at a temperature of about 480° C. and under a pressure of 75 lb. per sq. in. The gas is passed through the oil heated to a degree or two below its boiling-point under the required pressure, and then through a vertical steel tube 3 inches in diameter and 34 feet long, heated externally by a coil of copper wire embedded in a fireproof insulating compound, and through this coil, which is well lagged externally, an alternating electric current is passed, the magnitude of which can be conveniently controlled from an adjustable transformer so as to obtain any desired temperature. This heating current has a frequency of 60 alternations per second and a voltage of 60. Along the axis of the tube a platinum wire of 10 mils diameter is stretched from highly insulated supports at the ends of the tube. This central wire is connected to one pole of a very high frequency alternating oscillatory generator. The voltage of this oscillatory supply can be varied from 15,000 to 250,000 volts, and the frequency is several hundred thousand cycles per second with a current strength of from 3 to 5 ampères. The frequency is controlled by means of electric condensers of variable capacity and is provided with a specially designed adjustable spark gap. The high-voltage high-frequency discharge passes radially from the central platinum wire to the steel tube, which is earthed, and the electric current therefore flows at right angles to the direction of the stream of heated mixed petroleum vapour and gas which passes through the tube. The hydrocarbons are cracked by the combined action of the high temperature, pressure, and oscillatory discharge, and the resulting products pass out at the end of the tube into a dephlegmator, where the condensible liquids are collected and the non-condensible gases, consisting of methane and hydrogen (or, if steam is used, carbon monoxide), pass on, and are either used again for saturating with oil vapour or are burnt under the oil still. The whole of the apparatus is essentially of simple and substantial design, and is readily built and installed, whilst it shows very small depreciation as compared with the ordinary cracking equipment. No separation of carbon occurs. An installation dealing with 1440 gallons of kerosene per 24 hours has already been worked. The kerosene had a specific gravity of 0·81, and 78% was converted into a distillate of sp. gr. 0·751. The length of the 3 in. diameter steel tube in this plant was 10 feet. The yield of spirit was found to be proportional to the length of the tube and to increase with the frequency of the oscillating discharge and with the temperature. A plant is now being erected to deal with 60,000 gallons of kerosene in 24 hours, the cracking tube having a length of 34 feet as referred to above. It is estimated that the cost of electrical energy per gallon of oil treated is 0·4 cent. The cost of the hydrogen or methane used is not stated. No results of detailed tests of the kerosene used and of the cracked spirit obtained are given, and no commercial demonstration of the process has yet been made.

A paper on the preparation of toluol by cracking solvent naphtha in the presence of blue gas has been published by G. Egloff,[35] and a paper on solvent gasolene obtained by cracking heavy kerosene or other heavy oil has been contributed by C. O. North.[36]

ALCOHOL AS A MOTOR SPIRIT.

No review of recent advances in the cracking of oil for the manufacture of motor spirit would be complete without a reference to the proposals which have recently come to the front for the substitution or partial substitution of alcohol or mixtures of alcohol with either ether or benzol for petrol. These alcohol mixtures have long been employed in France and Germany and more recently in South Africa for motor purposes. A very important paper on this subject was read by W. R. Ormandy, on Nov. 19, 1918, before the Institution of Petroleum Technologists. The great advantage to be expected from the use of alcohol is that it can be produced in unlimited quantities and quite independently of all petroleum supplies, whilst provided that the Government will allow it to be sold duty free in the denatured condition it can be supplied at a price very considerably below that at which the great petroleum companies are at present prepared to sell petroleum spirit. It is true that when once the supply of industrial alcohol becomes established, the prices of petrol may, and probably will, be lowered to such a figure as to undersell the alcohol. Such a policy on the part of the petroleum producers will undoubtedly ruin any undertakings concerned in the manufacture of industrial alcohol, unless motor users determine to support such undertakings by purchasing alcohol at a moderate price and refrain from buying the cheaper petrol. If motor users do not follow this course, but for a temporary advantage buy the cheap petrol, the industrial alcohol undertakings will collapse, and it is rather more than probable that the price of petrol will then be found to rise again to much above the price at which industrial alcohol can be sold at a profit. It is only by a far-sighted policy on the part of the motor users, by which they will enter into contracts to purchase alcohol at some fixed price over a term of years, that the destructive competition between alcohol and petrol can be defeated.

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[35] *J. Ind. Eng. Chem.*, 1918, 10, 8; *J.*, 1918, 116A.

[36] *J. Ind. Eng. Chem.*, 1917, 9, 1038; *J.*, 1918, 3A.

Recovery of Waste Oil.

Economy in the use of oil necessitated by war conditions has caused an increasing use of de-oiling plants for the recovery of oil from cotton waste, overalls, and other materials, and incidentally the recovery of the cotton waste and the cleaning of the overalls; amongst these the Tern de-oiling plant has proved very satisfactory.

The apparatus devised by J. L. Sands[37] for the cleaning and recovery of lubricating oil which has become deteriorated in use due to the admixture of water and dirt, has given very good results on the large scale.

Oil Production.

An important paper entitled "A New British Oil Industry," dealing with the distillation of the high ash containing deposits of cannel coals, torbanites, and black-band ironstones by low temperature methods, has recently been read before the Institution of Petroleum Technologists by Craig, Perkin, Berry, and Dunstan.[38] The chief circumstance which renders these proposals more difficult of realisation than those for the low temperature distillation of coal, is the uncertainty as to the quantity and uniformity of quality of the raw material which is available for treatment. On this account it appears very desirable that the problem of the low temperature distillation of coal on the large scale should first be solved. The experience gained in dealing with coal will then undoubtedly secure the best solution of the kindred but smaller problem of the treatment of these high ash containing waste fuel materials.

The low temperature distillation of coal has not yet been carried out on a scale suited to the magnitude of the supplies of the raw material with which it is finally proposed to deal. It is believed that the largest plant laid down for this purpose at present can only deal with 200 tons of coal per diem, although it is generally agreed that works capable of dealing with from 1000 to 2500 tons of coal per day would form the most satisfactory unit. In view of these facts, although the conclusion of the war will no doubt remove many difficulties which have been recently experienced in the erection of large units of plant, it appears that industrial undertakings dealing with the low temperature distillation of cannels, torbanites, and black-band ironstones will probably remain of subsidiary interest for some time to come.

A paper by T. F. Winmill on the low temperature distillation of inferior coals[39] is of interest in the above connection as tending to advise caution in carrying out such proposals as those subsequently put forward by Craig, Perkin, Berry, and Dunstan. Winmill, in fact, concludes that low temperature distillation cannot be made to pay on the value of the by-products alone, and hence is useless as a means of utilising waste fuels of high ash content.

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[37] Eng. Pat. 106165; *J.*, 19.

[38] *J. Inst. Pet. Tech.*, 1918, 4, 110: *J.*, 1918, 79R, 175A.

[39] *J.*, 1917, 912.

It was announced in April last[40] that the Ministry of Munitions had appointed a Committee under the presidency of Lord Crewe to consider the report of the Petroleum Research Department on the Production of Oil from Home Sources, and to advise to what extent and in what time it should be possible to carry out the proposals in that report.

At about the same time, the Council of the Institution of Petroleum Technologists also appointed a Committee to inquire into the possibility of employing cannel coal and allied substances available in Great Britain as a source of supply for motor spirit, fuel oil, and other products, and to formulate a scheme for the utilisation of these minerals.

Lord Crewe's Committee has reported as follows:[41]

1. The carbonisation of cannel and kindred substances recommended by the Petroleum Research Department is not practicable, and the Ministry of Munitions was justified in declining to assist.

2. The alternative policy of producing oil from cannel, &c., in existing vertical retorts on a limited scale until shown to be satisfactory, should be developed.

3. The erection of a battery of the Chiswick form of retorts was the right course as decided by the Ministry of Munitions. Thirty of these retorts were to be erected at Nottingham to compare results with those obtained at the Nottingham Gas Works where cannel coal is now being dealt with in existing gas works retorts which have been adapted for this purpose. This arrangement will permit of a comparison on the industrial scale between the two systems of carbonisation.

A few days before the issue of the above report, a report on the same subject was issued by the Committee of the Council of the Institution of Petroleum Technologists.[42] The general conclusion of this report is that 10,000 tons per day of cannel coal and allied minerals, much of which is now waste material, could be assembled for treatment, and from this a yield of 400,000 tons of crude oil per annum could be secured. This is equivalent to an average of 11·2% by weight of oil on the cannel coal, &c., distilled. It is to be inferred from this report that it is considered that this production of crude oil could be obtained at a satisfactory profit on the capital involved, provided that the utilisation of the by-products and residues is made a part of the scheme.' It is to be observed that (*a*) the committee does not recommend any special form of retort, on account of the fact that the materials to be treated vary widely in their character and in their behaviour under distillation, and (*b*) the committee strongly urge that the Government shall either maintain an experimental station at which the behaviour of retorts of provisionally approved design can be experimentally tested, or that they shall afford the Institution of Petroleum Technologists reasonable facilities for the erection of a testing station of its own.

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[40] *J.*, 1918, 158R. [41] *J.*, 1918, 325R. [42] *J.*, 1918, 326R.

From these two conclusions it is to be presumed that the Committee has not yet been able to formulate any very definite lines of procedure, for this cannot very well be possible until the type, dimensions, and numbers of the necessary retorts can be fixed. Thus on the whole both these reports are more in agreement with one another than might be supposed from a cursory inspection, whilst the termination of the war will largely remove all antagonisms of aims between private capitalists and the Government, by leaving a practically free hand to the former to carry out any views that commend themselves to them without being hampered by the necessarily vexatious war restrictions as to labour and the priority of supply of constructive material, more especially iron and steel.

No fresh information has been published with regard to the development of the English shale oil deposits in Dorset and Norfolk since the paper by Forbes Leslie on the Norfolk oil shales,[43] which possesses mainly a geological and prospecting interest.

As far as is known, the removal of sulphur from the distillate obtained from the English oil shales on a paying commercial basis still remains an unsolved problem. If this desulphurisation can be carried out, probably a big field for the exploitation of these shales exists.

PETROLEUM IN GREAT BRITAIN.

During the past two years public attention has been constantly directed to the possibility or probability of the existence of natural oil fields in contradistinction to oil shales in Great Britain, and more particularly in England. In January 1917, a paper on the occurrence of petroleum in England was read by W. Forbes Leslie, who concluded that there is still a bulk of petroleum commensurate with that which has already been absorbed by the overlying shale beds and sandstones of the upper oolitic horizon, whilst W. H. Dalton[44] considers that there are no prospects of petroleum in the British Isles of value commensurate

[43] *J. Inst. Pet. Tech.*, 1916, 3, 3.

[44] *J. Inst. Pet. Tech.*, 1917, 4, 37 *J.*, 1918, 116A.

with the cost of search and exploitation. The discussion which followed this paper showed the wide diversity of opinion which exists on this subject. In the meanwhile the question is being submitted to the arbitrament of the drill, as the following records of Government action show.

On March 31, 1918, it was stated in Parliament[45] that applications by three firms to bore for petroleum were under consideration. Any agreements made would give exclusive rights to bore within certain defined areas. On August 1, 1918, the Minister of Blockade introduced a Bill respecting the boring for petroleum, the main object of which was to protect any possible oil fuels from the wasteful effect of indiscriminate boring, but leaving all controversial questions as to ownership, &c., to be settled after the war. The Bill passed the Commons on August 5, 1918.

Since then, boring operations have commenced in Derbyshire, whilst preparations are being made for boring for oil in the Chesterfield district,[46] and machinery and skilled labour has been brought from the United States. It is considered that in this district oil is most likely to be found at about 2000 ft., but, if necessary, boring will be continued down to 4000 feet. Preparations are also being made to prospect in the Codnor Park and Pye Bridge districts. In a colliery at Pye Bridge a stream of oil was discovered in 1847 producing about 300 gallons daily. This source eventually ran dry.

PETROLEUM IN BRITISH POSSESSIONS.

H. M. S. Jack has published a paper on the development of the petroleum industry in Assam.[47] The oil obtained has sp. gr. 0·856 and is perfectly fluid at 82° F., but at 81° F. crystals of paraffin wax begin to form, and at 77° F. the oil becomes semi-solid. The oil is refined in Assam by distillation and refrigerating. Two grades of petrol are produced, having sp. gr. 0·710 and 0·750. There is a great difficulty in obtaining a market for this spirit, as the consumption for motor cars is at present small in India. The Assam Oil Company has, however, successfully developed a demand for petrol for illumination by means of air gas used with incandescent burners. The kerosene is largely absorbed by native demand for lamp oil. One of the products turned out by the refinery, for which there is a large sale, is the oil known as batching oil, sp. gr. 0·885–0·890, used for softening jute fibre to facilitate its manufacture into rope, &c.

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[45] *J.*, 1918, 136R.

[46] *J.*, 1918, 379R.

[47] *J. Inst. Pet. Tech.*, 1917, 3, 263.

The paraffin wax obtained from the oil is very hard, and possesses a high melting-point (140°–145° F.). The total waste in distillation amounts to 5%.

In a paper on the prospective oil fields of Barbados, E. H. C. Craig[48] states that there is every probability of a moderate production being maintained in the most favourable localities. The oil, which is a fairly high-grade petroleum of asphaltic base, is mobile and contains a good percentage of light oils

In 1916 an increase in the export of petroleum from Trinidad took place, and a general marked development of the industry occurred. Thirty-four successful new borings were made, and altogether ten companies were engaged in the industry. Refining is carried on to a limited extent, petroleum, kerosene, lubricating and fuel oils of a very diversified character being obtained. On March 11, 1918, it was stated in Parliament[49] that fourteen companies were then engaged in the Trinidad oil industry; 365 wells had been sunk and 146 were actually being worked during November 1917, with an output of upwards of 4,500,000 imperial gallons (presumably during that month). By far the larger part of these oil fields is already under licence or lease.

A new oil well with an initial flow of over 200 barrels a day has been struck in Dover township near Chatham, Northern Ontario,[50] whilst indications of oil have been observed in the Sudbury district. Many claims have been staked out and drilling is going on.

In South-western Ontario, at West Dover, Kent County, two valuable oil wells have been located,[51] one of which produces about three million cubic feet of gas and 400 barrels of oil per day.

Oil has been obtained from a boring at a depth of 1396 feet at Chertsey, Canterbury, New Zealand,[52] and it is considered probable that a flow of oil will be obtained at a depth of 2000 feet.

PETROLEUM UNDERTAKINGS ABROAD.

T. S. Masterson has recently[53] given a description of the oil-fields of Roumania from the time of their earliest exploitation, with notes on their geography, climate, communications, mining rights, land tenure, geology, state of development, methods of drilling adopted, labour resources, supply of mining material, and of the refining, storage, and transport of the oil.

A paper on the Russian petroleum industry and its prospects, by

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[48] *J. Inst. Pet. Tech.*, 1918, **4**, 68.

[49] *J.*, 1918, 115R.

[50] *J.*, 1918, 278R.

[51] *J.*, 1918, 319R.

[52] *J.*, 1918, 57R.

[53] *J. Inst. Pet. Tech.*, **4**, 79.

D. Ghambashidze,[54] contains a very detailed description of the various Russian oil-fields, and more especially of those of Baku. A large amount of detailed statistics as to output, prices, and the character of the oils obtained is given.

A company formed with American, Belgium, and Portuguese capital has been working petroleum in Angola since 1913.[55] Bores to the depth of one mile have been made near Loanda. There seems to be every indication of the existence of petroleum, but no gusher has yet been discovered.

[54] *J. Inst. Pet. Tech.*, 1918, **4**, 158.

[55] *Board of Trade J.*, Jan. 17, 1918 ; *J.*, 1918, 58R.